CHEMISTRY LIBRARY
Nov 16'56

JOURNAL
OF THE
INDIAN CHEMICAL SOCIETY

VOL. XXXIII AUGUST, 1956 No. 8

CONTENTS

PAGE

119. Monoterpenoids. Part I. A synthesis of (±)-cryptone.—By G. S. Krishna Rao and Sukh Dev 539
120. Synthetic approaches towards triterpenes.—By S. C. Bhattacharyya ... 545
121. Reduction of copper borate by hydrogen.—By S. K. Deb and M. H. Khundkar ... 555
122. Studies in vat dyes. Part V. The acyl derivatives of mono- and di-aminoanthraquinones using long chain fatty acids.—By R. D. Desai and R. N. Desai ... 559
123. Studies in sesquiterpenes. Part XIII. Syntheses of 4:5- and 4:8-dimethyleudalenes.—By G. S. Krishna Rao and Sukh Dev 561
124. Thermal decarboxylation of chlorobenzoic acids.—By S. S. Muhammed and Miss Aziz Siddiqui 570
125. Paper ionophoresis of some purines and pyrimidines.—By S. N. Mukherjee and (Late) A. R. Ghosh 573
126. Constituents of *Centalla asiatica*. Part I. Examination of the Ceylonese variety.—By S. C. Bhattacharyya 579
127. An analysis of the neutralisation curves of the colloidal acids. Part I.—By S. L. Gupta 587
128. Studies on 3-*o*-tolyl- and 3-*p*-tolyl-2:4-thiazolidiones.—By P. N. Bhargava, R. P. Rao and M. S. Sastry 596
129. Absorption and fluorescence spectra of chromones.—By S. K. K. Jatkar and B. N. Mattoo 599
130. Anodic phenomena in the electrolysis of silver salts. Part I. Formation of silver peroxynitrate.—By A N. Kappanna and Indra Dev Arya ... 605
131. Chemistry of aliphatic thiocarbamides. Part V. N:N:N′-trimethylthiocarbamide.—By Ranbir Singh 610
132. Studies on the Fries rearrangement. Part XVI.—By S. S. Tewari and Brajendra Nath Tripathi 613
133. The digestibility of cereal starches by Taka-diastase and pancreatin at different p_H and at 38.5° ± 0.01°.—By R. D. Patel and R. S. Patel ... 615
134. Condensation of aryldiazonium salts with reactive unsaturated compounds. Part VIII. Action of aryldiazonium chlorides with β-4-methoxy- and β-3:4-dimethoxybenzoylacrylic acids.—By Hari Shanker Mehra and Kunj Behari Lal Mathur 618
135. A note on the volumetric estimation of iodine in iodide.—By Arcot Viswanathan and Sankaranarayana Gireesan 621

PUBLISHED BY THE INDIAN CHEMICAL SOCIETY
92, UPPER CIRCULAR ROAD, CALCUTTA 9.

READY DELIVERY

"SIGCOL"

LABORATORY GLASSWARE

Made of

BOROSILICATE GLASS HAVING HIGH SILICA AND LOW ALKALI CONTENT WHICH ENSURES RESISTANCE TO THERMAL SHOCK AND CHEMICAL STABILITY

SARTORIUS

"SELECTA" BALANCES

Micro and Projection Types

CARL-ZEISS

REFRACTOMETERS

SPECTROPHOTOMETER

STEREO-MICROSCOPES

MUIRHEAD

POTENTIOMETER

"K-9"

TRIANGULAR BEAM

CIRCULAR ARRESTMENT

ANALYTICAL BALANCE

CAPACITY: 200 Gms. SENSITIVITY: $\frac{1}{10}$ Mgm. 5 Divisions throw of pointer for addition of 1 Mgm.

CARL-ZEISS

HAND SPECTROSCOPES

POLARISING MICROSCOPES

METAL MICROSCOPES

POLARIMETERS

MICRO-PHOTO CAMERAS

LEYBOLD'S

VACUUM PUMPS

HERAEUS- OVENS

JULIUS PETER- BOMB CALORIMETER

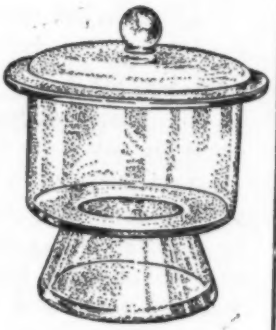
HOPPLER- VISCOMETERS

Distributors:

ADAIR, DUTT & Co. (INDIA) PRIVATE Ltd.

CALCUTTA MADRAS BOMBAY NEW DELHI

LATEST PRODUCTS OF THE "MM" Group



Desiccator.

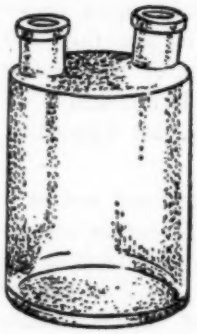
— NEUTRAL —
RESISTANCE HARD GLASS

In addition to their established range of Bakelite mouldings "MM" now offer Glass of especially high quality.

Measuring Cylinder.

Laboratory control ensures bulk output to uniform standards.

Calcium Tower.



Woulfe's Bottle.

Enquiries invited for all types of Scientific Glassware, Domestic Tableware, and Ink Bottles etc.

MODERN MOULDERS

14/2, OLD CHINA BAZAR ST., CALCUTTA-1.

Telephone:
Office: 22-3725

Information for Auth

1. All papers intended for publication in the Journal of the Indian Chemical Society should be addressed to the Hony. Secretary, Indian Chemical Society, 92, Upper Circular Road, Calcutta-9.

2. A paper will not normally be considered for publication in the Journal unless at least one of the authors or authors is (are) either a Fellow or an Associate member of the Society.

3. Communications which have appeared in any other journal shall not be published in this Journal unless this course is specially approved by the Council.

4. Normally an article or original paper should not exceed 15 foolscap pages. All papers should be submitted in typescript with double line and marginal spacings. Tables and foot-notes add considerably to the cost of printing ; authors are requested therefore not to use them unless necessary.

5. All papers should be carefully revised and should be absolutely in final form of printing. Positions for text-figures should be indicated. Authors are particularly requested to verify references. Authors are solely responsible for the factual accuracy of their papers.

6. Authors should note that the communications are meant for specialists in that field. Extensive review of literature should be avoided. Well known or previously published procedures followed in the experimental work should only be designated or referred to.

7. Periods of time (unless fractional) and quantities of material should be written in numerals. For economy the abbreviations, cm., c.c., ml., g., m.p., b.p., f.p., calc., exp., Fig., etc., should be used.

8. Authors are requested to enclose line drawings of the diagrams in their papers drawn in India ink on smooth white Bristol board. The drawings should be twice the size they will occupy in the Journal. Authors are particularly requested to reduce the number of diagrams and formulae to an absolute minimum. Organic structural formulae should be arranged to fill the space economically and arrows should be used horizontally or vertically, not diagonally, whenever possible.

9. The reference to literature should be given in brackets in the text and not as a foot-note or at the end and should conform to the normal usages of the *Journal* as regards order and punctuations, and to the abbreviations as given by Chemical Abstracts in its "List of Periodicals Abstracted". Thus, Name or names of authors, Name of Journal (abbreviated, with a single underline); year of publication; number of volume (double underline) and lastly page, e.g., Karrer and Schlieutz, *Helv. Chim. Acta*, 1934, **17**, 7.

The words and lines that will appear in italics in print should be underlined.

10. Authors are expected to be familiar with the normal rules of nomenclature but in case of doubt may refer to "Modern Chemical Nomenclature (Smith, *J. Chem. Soc.*, 1936, 1067).

11. New compounds should be indicated by underlining the name at its first mention (excluding Headings) in the experimental section and by giving analytical results in the form: "Found:———; ———. ——— requires ——— per cent". Analytical results for compounds which have been previously known should be given in the form: "Found:——; ———. Calc. for———: ———; ——."

12. Every paper should be accompanied by a short abstract giving briefly the objects of the investigation, the results obtained and their bearing on chemical knowledge in general. It should be such as to enable any chemist to obtain a clear idea of the investigation and normally should not exceed 250 words.

13. The address to which the proofs are to be sent should be written on every paper. One slip-proof or if possible a page-proof will be sent to authors, which should be returned whithin a week to the Hony. Secretary, failing which it will be directly printed.

14. Authors will get 50 copies of reprints free of charge and extra 25 copies on payment of Re. 1/- per page. Extra copies of reprints over 75 copies will be charged at Rs. 5/- per page. Cost of paper and binding extra. If extra copies are required, the author should intimate the Hony. Secretary, at the time of returning the corrected proofs. It would be desirable to inform him when the manuscript is sent.

15. **Notes will be given priority in publication.**

Change of address should be immediately intimated to the office.

No claims will be allowed for copies of Journal lost in the mail or otherwise, unless such claims are received within 90 days of the date of issue.

	Inland rates.	Foreign rates.	
		Sterling area	Dollar area
Cost of Single Issue	**Rs. 3**		
Annual Subscription	**,, 20 (for Fellows)**	**20**	**28**
	,, 24 (for Subscribers)	**28**	**32**
	,, 28 (Composite)	**34**	**40**

Rates of Advertisement

In Ordinary Pages:
(Single insertion)

Full Page	... ...	Rs. 40/-
Half Page	... ...	,, 25/-
Quarter Page	... ...	,, 15/-

In Cover Pages:

Cover (Back) Full	...	Rs. 100/-
,, ,, Half	...	,, 60/-

In special positions:

Page facing first reading matter	...	Rs. 70/-
Page facing last page of reading matter	...	,, 60/-

Second and Third Pages:

Full Page	...	Rs. 70/-
Half Page	...	,, 40/-
Quarter Page	...	,, 25/-

Page facing inside front cover	...	,, 50/-
Page facing inside back cover	...	,, 50/

Closing date for advertising materials: 7th of the previous month.

The above rates apply also to the Industrial and News Edition.

10% *Rebate allowed in cases of six consecutive full and half page insertions.*

All communications are to be addressed to:

The Hony. Secretary,
INDIAN CHEMICAL SOCIETY
92, Upper Circular Road, Calcutta-9.

Ex: M/S BELLINGHAM & STANLEY LTD., ENGLAND

PULFRICH (CRITICAL ANGLE) REFRACTOMETER

IMPROVED TYPE

PULFRICH REFRACTOMETER.

This instrument has recently been redesigned and incorporates the results of modern research on the subject.

Refractive index measurements can be made from 1.3 to 1.85 and if equipped with the special cell the range can be extended to 1.25-1.95 Accuracy 0.00002

All necessary accessories including different sources of light are available for advanced measurements with this instrument.

OTHER INSTRUMENTS

Abbe, pocket, sugar & Oil (Butter), immersion, pan and pipeline, projection and interference refractometers, polarimeters and saccharimeters ; Spectrometers ; spectrographs ; Interferometers etc.,

SOLE AGENTS IN INDIA :

TOSHNIWAL BROTHERS PRIVATE LTD.

198, Jamshedji Tata Road,
FORT, BOMBAY-1.

Delhi Office :
3/7, Mutiny Memorial Road,
NEW DELHI-1.

Madras Office :
9, Blackers Road,
MADRAS-2.

[Jour. Indian Chem. Soc., Vol. 33, No. 8, 1956]

MONOTERPENOIDS. PART I. A SYNTHESIS OF (±)-CRYPTONE *

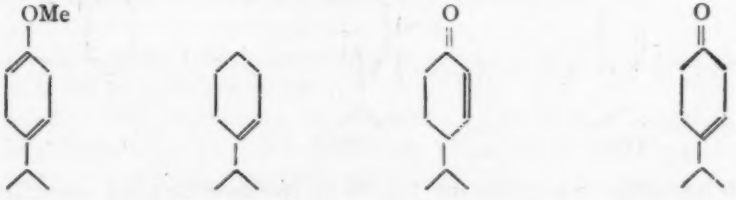
By G. S. Krishna Rao and Sukh Dev

An improved procedure for the preparation of (±)-cryptone has been described. In an attempt to find an alternative route to this ketone, some interesting observations on the *tert.*-butyl chromate oxidation of a few alkyl*cyclo*hexenes have been made.

Cryptone or 4-*iso*propyl-Δ^2-*cyclo*hexen-1-one (III) was first described by Wallach (*Annalen*, 1905, **343**, 30) as a degradation product of β-phellandrene. Latter on it has been found to occur in Nature (Cahn *et al.*, *J. Chem. Soc.*, 1931, 1366; Berry *et al.*, *ibid.*, 1937, 1448; Wienhaus and Striegler, Schimmel's Report, 1937, p. 91).

To us cryptone appeared to be a suitable starting material for a synthesis of cadinene, and with this end in view we have studied, as a first step, the preparation of (±)-cryptone. With the publication of a modification of the Birch reduction (*J. Chem. Soc.*, 1944, 430; *Quart. Rev.*, 1950, **4**, 69) by Wilds and Nelson (*J. Amer. Chem. Soc.*, 1953, **75**, 5360), the previously studied route (Talukdar and Mukherji, *Science & Culture*, 1952, **18**, 150; Bhati, *Curr. Sci.*, 1952, **21**, 314) has been reinvestigated and a procedure developed for the preparation of cryptone.

Lithium and alcohol reduction of *p-iso*propylanisole in liquid ammonia afforded the corresponding dihydroanisole (I) in 90% yield; a small amount (9%) of a lower boiling fore-run, which had been identified as 1-*iso*propyl-Δ^1-*cyclo*hexene (II), could also be isolated. The dihydro compound (I) was rather unstable; a seven-month old sample on redistillation yielded only 50% as the distillate, and this showed a maximum at 224 mμ, indicating that on storage some isomerisation to a conjugated isomer had taken place. The 2:5-dihydro-4-*iso*propylanisole (I) on treatment with 2:4-dinitrophenylhydrazine reagent furnished the corresponding derivative of cryptone in 87% yield. Similarly, the cryptone semicarbazone could be directly prepared from (I) in 78% yield. The regeneration of cryptone (III) from its semicarbazone has been described by Galloway, Dewar and Read (*J. Chem. Soc.*, 1936, 1595) and Cooke and Macbeth (*ibid.*, 1938, 1408); the ketone could also be generated from its 2:4-dinitrophenylhydrazone by Robinson's method (*Nature*, 1954, **173**, 541), but the recovery was poor.



(I) (II) (III) (IV)

* The experimental investigations embodying the results reported in the present paper were communicated to the Government of India in the form of a progress report of one of us (G.S.K.) on October 4, 1954. Also see Soffer and Jevnik, *J. Amer. Chem. Soc.*, 1955, **77**, 1003; Bhati, Ann. Rep. Indian Inst. of Science, Bangalore, 1954, p. 53.

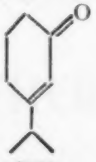
Treatment of (I) with aqueous hydrochloric acid in dioxane afforded a ketonic material which from its ϵ value (7,380) at λ_{max} (227 mμ) indicated that the product was contaminated with the $\beta\gamma$-isomer (IV) to the extent of about 40%. Filtration of this material through activated alumina (Basic/I) or its digestion with anhydrous oxalic acid in ethanol (Fieser, *J. Amer. Chem. Soc.*, 1953, **75**, 5421) did not shift the equilibrium in favour of the $a\beta$-isomer. A slight improvement in the cryptone content was achieved, when the product was treated according to the method of Barton *et al.* (*J. Chem. Soc.*, 1949, 1771; Johnson *et al.*, *ibid.*, 1954, 1302). These experiments indicate that the direct preparation of pure cryptone from the enol-ether (I) is not feasible (cf. Birch, *ibid.*, 1946, 593).

The enol-ether (I) on treatment with Girard "P" reagent could be converted into the ketonic fractions to the extent of only 30%, and this material from the light absorption data was computed as an 1 : 1 mixture of (III) and (IV).

tert.-*Butyl Chromate Oxidations*

As an alternative to the above procedure for the synthesis of (±)-cryptone, the oxidation of 3-*iso*propyl-Δ^1-*cyclo*hexene (V) by *tert.*-butyl chromate was investigated. This reagent has been shown (Oppenauer and Oberrauch, *Anales asoc. quim. Argentina*, 1949, **37**, 240; *Chem. Abs.*, 1950, **44**, 3871; Inhoffen *et al.*, *Chem. Ber.*, 1951, **84**, 87; Heusler and Wettstein, *Helv. Chim. Acta*, 1952, **35**, 289; Dupont and Cow, *Bull. soc. chim.*, 1953, **20**, 60; Ezchinazi, *Perf. & Ess. Oil Rec.*, 1953, **44**, 243) to be capable of oxidising an allylic methylene group to the corresponding carbonyl derivative. However, 3-*iso*propyl-Δ^1-*cyclo*hexene, instead of yielding the expected cryptone (III), furnished the isomeric $a\beta$-unsaturated ketone (VI). The structure of the product was confirmed by its light absorption data and a comparison of the melting points of the derivatives of the unsaturated (VI) and the corresponding reduced ketones. The fact that the starting material, as prepared by the method of Biggerstaff *et al.* (*J. Org. Chem.*, 1954, **19**, 934), was essentially (V), was established by its comparison with an authentic sample of 1-*iso*propyl-Δ^1-*cyclo*hexene (II). It became apparent that the olefin (V) rearranged to the hydrocarbon (II) during the oxidation step; this was confirmed by carrying out the *tert.*-butyl chromate oxidation of 1-*iso*propyl-Δ^1-*cyclo*hexene (II), when the same ketone (VI) could be isolated in about the same yield.

(V)



(VI)

(VII)

It is interesting to note that the *tert.*-butyl chromate attacked essentially the C_3-methylene group, rather than the C_6-position : this is in direct contrast to the attack by other allylic reagents which seek preferentially the carbon atom which is next to the more-substituted end of the ethylenic linkage (Mousseron *et al.*, *Compt. rend.*, 1947, **224**, 1062, 1230; Borgwardt and Schwenk, *J. Amer. Chem. Soc.*, 1934, **56**, 1185; Urion, *Compt. rend.*, 1934, **199**, 363; Linstead, *Ann. Rep. Chem. Soc.*, 1937, **34**, 241). This preferential

attack by *tert*-butyl chromate was further borne out by the oxidation of 1-methyl-Δ^1-*cyclo*hexene, when 3-methyl-Δ^2-*cyclo*hexen-1-one (VII) was isolated as the chief product of oxidation. This method of preparation of 3-alkyl-Δ^2-*cyclo*hexen-1-ones compares favourably with the previous methods (Mousseron and Winternitz, *Bull. soc. chim.*, 1945, *v*, **12**, 71; Woods *et al.*, *J. Amer. Chem. Soc.*, 1949, **71**, 2028; Birch, *J. Chem. Soc.*, 1946, 593; Birch and Mukherji, *ibid.*, 1949, 2531) which involve many steps.

Experimental

All melting and boiling points are uncorrected. Petroleum ether refers to the fraction of b.p. 40°-60°. All solvent extracts were finally dried over sodium sulphate. The light absorption measurements were carried out in 95% ethanol on a Beckman DU spectrophotometer.

*p-iso*Propylanisole was prepared by the methylation of *p-iso*propylphenol with dimethyl sulphate in alkali according to the directions of Bert (*Bull. soc. chim.*, 1925, *iv*, **37**, 1399); b.p. 104-105°/24 mm., n_D^{28} 1.5015, yield 93-97%.

Reduction of p-iso*Propylanisole*.—To a solution of *p-iso*propylanisole (15 g., 0.1 *M*) in dry ether (50 c.c.), placed in an one-litre three-necked flask, liquid ammonia (250 c.c.) was cautiously introduced under anhydrous conditions. The mixture was stirred and lithium pieces (4.6 g, 0.65 g. atom) were introduced during 10 minutes. Stirring was continued for another 10 minutes and then absolute ethanol (35 c.c.) was let in during 30 minutes with efficient stirring. The ammonia was allowed to evaporate off overnight and the residue carefully diluted with ice water (400 c.c.). The product was taken up in ether, washed with brine and dried. The solvent was stripped off and the residue (15 g.) precisely fractionated to give two cuts: (*i*) b.p. 55°-102°/23 mm., n_D^{28} 1.4600, yield 1.13 g. and (*ii*) b.p. 102-103°/23 mm., n_D^{28} 1.4765, yield 13.7 g.

The first fraction on rectification furnished a hydrocarbon (1.0 g.), b.p. 145°/684 mm., n_D^{28} 1.4585. This was identified as 1-iso*propyl*-Δ^1-cyclo*hexene* (II) from a comparison of its physical properties with an authentic sample (*vide infra*) and the preparation of its *nitrosochloride*. A mixture of the hydrocarbon (0.4 g.), ethyl nitrite (0.5 c.c.) and glacial acetic acid (0.5 c.c.) was well-chilled (ice-salt bath) and treated with HCl (A.R., 0.5 c.c.) during 5 minutes. The reaction mixture was stirred for 10 minutes more and left aside for 30 minutes, when a white crystalline solid (0.2 g.) separated. This was crystallised from benzene-ethanol mixture to afford white crystalline needles, m.p. 130°; mixed melting point with an authentic sample of the nitrosochloride, prepared as above from a sample of 1-*iso*propyl-Δ^1-*cyclo*hexene (*vide infra*), was not depressed (Mallison, *Annalen*, 1908, **360**, 69 reports m.p. 129°).

The second fraction represented the required 2:5-*dihydro*-4-iso*propylanisole* (I). A mixture of this product (1 g.), ethanol (70 c.c.), 2:4-dinitrophenylhydrazine (1.3 g.) and HCl (conc., 1 c.c.) was refluxed for 5 minutes. After several hours at room temperature, the crude *cryptone* 2:4-*dinitrophenylhydrazone* (1.82 g., 87%), m.p. 126-31°, was collected. It was recrystallised from benzene-ethanol mixture as orange-red flakes, m.p. 135° (Gillespie and Macbeth, *J. Chem. Soc.*, 1939, 1532, report m.p. 130-131° for the *dl*-cryptone 2:4-dinitrophenylhydrazone). [Found: N, 17.7. Calc. for $C_{15}H_{18}O_4N_4$: N, 17.6 per cent],

A mixture of 2:5-dihydro-4-*iso*propylanisole (0.4 g.) was added to a solution of semicarbazide hydrochloride (0.5 g.) in water (2 c.c.) containing pyridine (0.2 c.c.); sufficient alcohol was added to just get a clear solution. This was refluxed for ½ hour and the crystalline material collected after allowing it to stand for 24 hours in a cooling chamber. The product (0.4 g., m.p. 174-78°) was recrystallised from ethanol as white plates of *cryptone semicarbazone*, m.p. 187° (Gillespie and Macbeth, *loc.cit.*, report m.p. 188°).

For the preparation of the above derivatives in good yield, it is necessary to use the 2:5-dihydro-4-*iso*propylanisole immediately after its preparation. A seven-month old sample after distillation had b.p. 105-107°/25 mm., n_D^{28} 1.4770; λ_{max} 224 mμ (ε, 5500).

Regeneration of Cryptone from its 2:4-Dinitrophenylhydrazone.—The 2:4-dinitrophenylhydrazone (1.0 g.) was heated on the steam-bath with formic acid (90%, 8 c.c.) for one hour and then the acid was neutralised by the portion-wise addition of copper carbonate (12 g., 30 minutes). The product was then diluted with water and steam-distilled. The steam-distillate (100 c.c.) was extracted with ether (10 c.c. × 3), washed with brine and dried. The solvent was removed, when a pale yellow residue (0.15 g.), b.p. 110°/24 mm. was left. This immediately yielded the cryptone 2:4-dinitrophenylhydrazone on treatment with the reagent.

Hydrolysis of 2:5-Dihydro-4-isopropylanisole (I).—To a solution of the enol-ether (1 g.) in dioxane (pure, 30 c.c.) HCl (6 *N*, 3.4 c.c.) was added and maintained at 10° ± 2° with stirring for 2 hours. This was diluted with water (120 c.c.) and extracted with ether (10 c.c × 4). The combined extracts were washed with aqueous sodium bicarbonate (10%, 20 c.c.), brine (10 c.c. × 2) and dried. The solvent was removed and the residue fractionated to yield a colorless liquid, b.p. 110°/24 mm., n_D^{27} 1.4750, yield 0.46 g. (50%). Light absorption: $\lambda_{max.}$ 227 mμ (ε, 7380) (Cooke and Macbeth, *loc.cit.*, report $\lambda_{max.}^{ition}$ 226.3 mμ, ε 12,590 for pure *l*-cryptone].

The above product (0.3 g.) in chloroform (4 c.c.) was treated with dry HCl gas for 1 hour at 0° (Barton *et al.*, *loc. cit.*). On working up as usual (Johnson *et al.*, *loc. cit.*), colorless distillate (0.2 g.) was obtained, b.p. 110°/24 mm., n_D^{28} 1.4790, $\lambda_{max.}$ 227 mμ (ε 8160).

A mixture of the enol-ether (I, 1.52 g.), alcohol (10 c.c.), glacial acetic acid (1 c.c.) and Girard reagent "P" (2 g.) was refluxed for 1½ hours. The product was worked up as described by Sterrett (Guenther, "The Essential Oils", D. Van Nostrand Co. Inc., New York, 1949, Vol. II, p. 816) by pouring into ice water (130 c.c.) containing sodium carbonate (0.8 g.). After removal of the non-ketonic material (apparently the starting enol-ether; 0.7 g., b.p. 102°/24 mm.) with ether, the clear aqueous part was treated with dilute sulphuric acid (20%, 3 c.c.) and after 2 hours at room temperature it was worked up by extraction with ether to yield a ketonic material (0.45 g.), b.p. 105°/24 mm., $n_D^{27.5}$ 1.4730, $\lambda_{max.}$ 227 mμ (ε, 6510).

3-iso*Propyl*-Δ^1-cyclo*hexene* (V) was prepared essentially by the method of Biggerstaff *et al.* (*loc. cit.*), but the yields in our hands were superior. To a refluxing solution of 3-bromo*cyclo*hexene (22.4 g., Zeigler *et al.*, *Annalen*, 1942, **551**, 80) in dry ether (30 c.c.) was added a solution of *iso*propylmagnesium bromide (from Mg 6.4 g., *iso*propyl bromide 40 g. and ether 100 c.c.) during one hour. The refluxing was continued for

another 2 hours and the reaction mixture left aside overnight. This was then treated with a solution of ammonium chloride (20 g.) in water (50 c.c.) during 30 minutes with stirring. The solvent layer was separated and the aqueous phase extracted with ether (20 c.c. × 3). The combined extracts were washed with brine and dried. The solvent was removed (column) and the residue fractionated to yield the desired product as a colorless liquid, b.p. 88-90°/100 mm., n_D^{22} 1.4555, yield 11.8 g. (70%).

The *nitrosochloride* was prepared, as described above, for the isomeric hydrocarbon (II). The product on recrystallisation from benzene-alcohol mixture came out as fine white needles, m.p. 155°. (Found: N, 7.1. $C_9H_{16}ONCl$ requires N, 7.38 per cent).

3-iso*Propyl*-Δ^2-cyclo*hexen*-1-*one* (VI): (*i*) *From* 3-iso*Propyl*-Δ^1-cyclo*hexene* (V). —*tert.*-Butyl chromate solution was prepared from chromic anhydride (16 g., 0.16 *M*), anhydrous *tert.*-butanol (44 c.c.) and CCl_4 (124 c.c.) according to the direction of Heusler and Wettstein (*loc. cit.*). The solution was concentrated to 84 c.c. and then diluted with glacial acetic acid (25 c.c.) and acetic anhydride (10 c.c.). This reagent was added to the above hydrocarbon (5 g., 0.04 *M*) in dry CCl_4 (28 c.c.) during 45 minutes at 70°-75° with stirring. The reaction mixture was stirred at this temperature for another 2½ hours and then the green product left aside overnight. To this, aqueous oxalic acid (16 g. in 160 c.c. of water) was let in during one hour with stirring at room temperature; this was followed by the addition of solid oxalic acid (12 g.) during 15 minutes. The pale yellow CCl_4 layer was separated and the aqueous phase extracted with CCl_4 (20 c.c. × 3). The combined solvent layers were washed neutral with water (20 c.c.), aqueous sodium bicarbonate (10%, 40 c.c. × 2) and dried. The solvent was flashed off and the pale yellow residue filtered through a column of activated alumina (Basic/1; 30 g.); this was washed with petroleum ether (180 c.c.). This treatment left the coloured impurity as a violet-green band on the column. The almost colorless petroleum ether eluate was distilled (column) to remove the solvent; the residue was fractionated to yield a colorless liquid, b.p. 112-13°/20 mm., $n_D^{27.5}$ 1.4845, yield 2.1-2.4 g. Light absorption: $\lambda_{max.}$ 235 mμ (ε, 10,000) (Woods *et al.*, *loc.cit.*, record b.p. 59-60°/0.3 mm., n_D^{25} 1.4842; cf. Roy, *Science & Culture*, 1953, **19**, 156).

The crude 2:4-*dinitrophenylhydrazone* (HCl method), m.p. 138°-145°, was obtained in 80% yield. Recrystallisation from benzene-petroleum ether mixture furnished scarlet-red prisms, m.p. 154-55° (Woods *et al.*, *loc.cit.*, record m.p. 154.4°−155.5°).

The *semicarbazone* was prepared by the pyridine method and after three crystallisations from ethanol furnished white plates, m p. 184° (Woods *et al.*, *loc.cit.*, report m.p. 179-179.5°). A mixed melting point determination with (±)-cryptone semicarbazone gave a sharp depression.

When the unsaturated ketone (1 g.) in ethanol (12 c.c.) was hydrogenated in the presence of pre-reduced Pd—$CaCO_3$ catalyst (0.5 g., 5%), hydrogen equivalent to one ethylenic linkage was readily (15 minutes) taken up, and the reduction came to a close. The reduced material was worked up in the usual manner to yield 3-iso*propyl*cyclo*hexanone* as a colorless, mobile liquid, b.p. 200°-205°/684 mm., n_D^{25} 1.4560 (Woods *et al.*, *loc. cit.*, record b.p. 50-51°/1 mm., n^{20} 1.4540). Its 2:4-*dinitrophenylhydrazone*

(HCl method) was obtained as golden yellow flakes from benzene-petroleum ether mixture, m.p. 139° (Woods *et al.*, *loc. cit.*, report m.p. 139-40°). The *semicarbazone* was obtained as white leaflets on two crystallisations from ethanol, m.p. 190° (Woods *et al.*, *loc. cit.*, record m.p. 194.5-95° ; Whitmore and Pedlow, *J. Amer. Chem. Soc.*, 1941, **63**, 758, record m.p. 189 90°).

(*ii*) *From* 1-iso*Propyl*-Δ^1-cyclo*hexene* (II).—The hydrocarbon was prepared by the action of *iso*propylmagnesium bromide on *cyclo*hexanone and subsequent dehydration of the carbinol with a trace of iodine (Mosher, *ibid.*, 1940, **62**, 552). The material had b.p. 145°/684 mm., n_D^{26} 1.4590 (Mallison, *loc. cit.*, record n_D^{20} 1.4606) and afforded a *nitrosochloride*, m.p. 129-130°, prepared as described above.

The olefin (1.98 g., 0.016 *M*) was oxidised with *tert.*-butyl chromate reagent as described above for (V). The purified ketone (VI), b.p. 112-15°/22 mm., $n_D^{27.5}$ 1.4850, was obtained in 40% yield. The 2:4-*dinitrophenylhydrazone*, m.p. 155°, and the *semicarbazone*, m.p. 183-84°, did not depress the melting points of the corresponding derivatives of the ketone (VI), obtained from the 3-*iso*propyl-Δ^1-*cyclo*hexene (V).

Oxidation of Methyl-Δ^1-cyclo*hexene*: *Isolation of* 3-*Methyl*-Δ^2-cyclo*hexen*-1-*one*. —When Δ^1-methyl*cyclo*hexene (3.8 g., 0.04 *M*) was oxidised with *tert.*-butyl chromate reagent, as described for (V), the unsaturated ketone was isolated in 25% yield as a colorless liquid, b.p. 100°-104°/30 mm., n_D^{26} 1 4840; 2:4-*dinitrophenylhydrazone*, bright red prisms (benzene), m.p. 178° ; *semicarbazone*, white prisms (pyridine-ethanol method ; crystallised from ethanol), m.p. 201° (Woods *et al.*, *loc.cit.*, record b.p. 40°/0.8 mm., n_D^{20} 1.4945 ; 2:4-dinitrophenylhydrazone, m.p. 177-78° ; semicarbazone, m.p. 198 5–99.5°).

The authors take this opportunity to thank the Government of India for the award of a senior scholarship to one of them (G.S.K.R.).

Department of Organic Chemistry,
Indian Institute of Science,
Bangalore.

Received December 15, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 8, 1956]

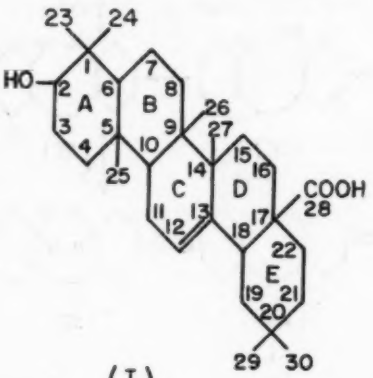
SYNTHETIC APPROACHES TOWARDS TRITERPENES

By S. C. Bhattacharyya

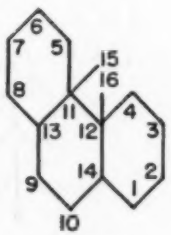
Methods for the preparation of a phenanthrenoid hydrocarbon with two vicinal angular methyl groups and of a similar phenanthrenoid ketone have been established. Preparation of two isomeric keto-octalenes has also been described.

Triterpenes like β-amyrin, oleanolic acid, etc. form a very important group of plant products. Synthetic approaches in this group have been mostly confined to the synthesis of the dehydrogenation products of these compounds.

The most conspicuous part of the ring structure of a triterpene like oleanolic acid (I) is the hydrogenated phenanthrene skeleton (rings B, C and D) with two vicinal angular methyl groups, No. 26 and 27 in positions 9 and 14 in the central part of the molecule.



(I)

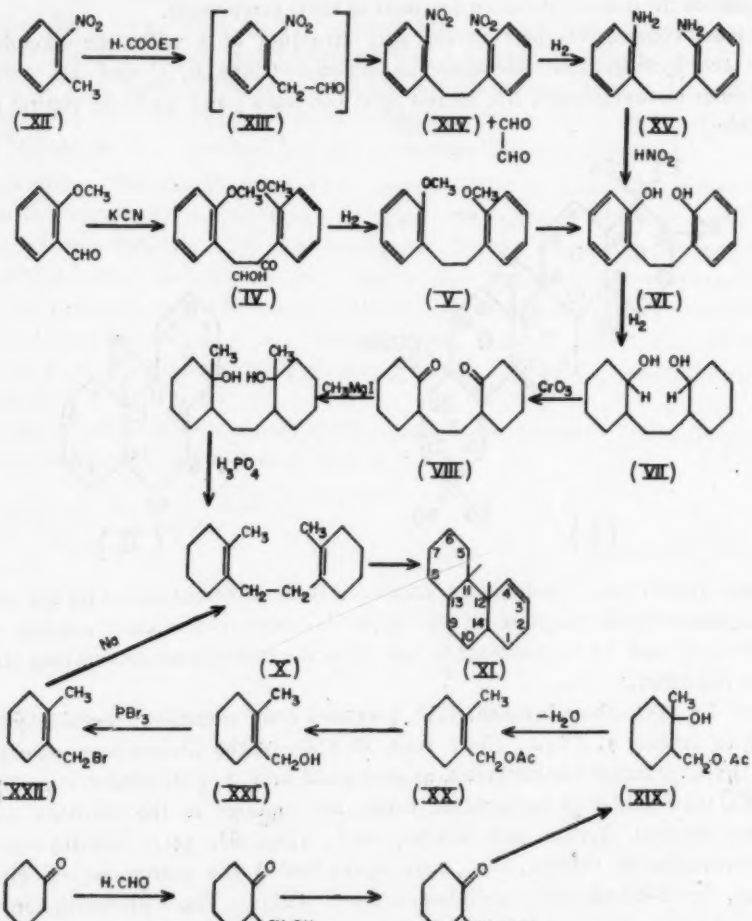


(II)

In this paper, as a preliminary measure, three different routes for the synthesis of a hydrophenanthrene structure of the type (II) with two vicinal angular methyl groups No. 15 and 16 in positions 11 and 12 of the hydrophenanthrene ring-structure have been described.

Route I: Dimethoxybenzoin, (IV), prepared from *o*-methoxybenzaldehyde (III) according to Irvine (*J. Chem. Soc.*, 1901, **79**, 668), on the Clemmensen reduction or catalytic hydrogenation was converted in good yield into 2 : 2′-dimethoxy-1 : 2-diphenylethane (V), this method of preparation being far superior to the methods described by earlier workers (Irvine and Moodie, *ibid.*, 1907, **91**, 54); demethylation with pyridine hydrochloride (Mason, *ibid.*, 1947, 251) afforded the corresponding diphenolic compound, 2 : 2′-dihydroxy-1 : 2-diphenylethane (VI). The dinitrodiphenylethane derivative (XIV), prepared from *o*-nitrotoluene (XII) and ethyl formate (Lapworth, *ibid.*, 1901, **79**, 1275), on hydrogenation to the diamino compound (XV), followed by diazotisation and heating, also furnished the same diphenolic compound (VI) in satisfactory yield. On hydrogenation under pressure (VI) was converted into the crystalline diol (VII) which on oxidation with chromic acid afforded the solid diketone (VIII). The

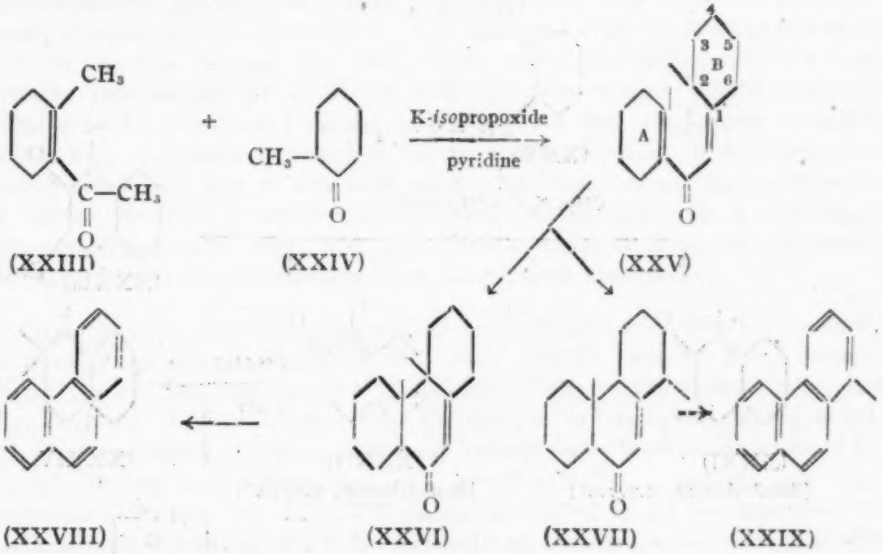
latter reacted with two moles of magnesiummethyl iodide to form the crystalline ditertiary alcohol (IX), which in the next stage, through cyclodehydration with phosphoric acid (Linstead, *ibid.*, 1936, 470, 477), was converted into the desired phenanthrenoid compound, 11: 12-dimethyl-$\Delta^{5:6}$-dodecahydrophenanthrene (XI), formed, presumably, through the intermediate diene (X). The yields in all the stages were excellent, being almost quantitative or nearly so. The cyclic structure of (XI) was proved as, (*i*) it absorbed one mole of hydrogen, indicating the presence of one double bond, and (*ii*) dehydrogenation with selenium produced phenanthrene. The position of the double bond in (XI) is provisional.



Route II: This route has not been worked out in all the details as in the case of route I. In certain stages the intermediates were not isolated in analytically pure

state. However, the ultimate phenanthrene derivative (XI) and the diene (X) could be successfully prepared by this method also, the actual isolation of the diene (X) in this case being possible. The acetate (XVIII) of the keto-alcohol (XVII), prepared from *cyclo*hexanone and formaldehyde (Bodendorf, *Ber.*, 1943, **76**, 641), on reaction with one mole of magnesiummethyl iodide, keto-group reacting preferentially, formed the tertiary alcohol (XIX); dehydration, followed by hydrolysis, furnished 2-methyl-Δ^1-*cyclo*hexenyl carbinol (XXI). The bromide (XXII) of this allylic alcohol was converted into the diene (X) by treatment with sodium, as in the case of the preparation of diallyl (Vogel, "Practical Organic Chemistry", 1941, p. 453); cyclisation with phosphoric acid afforded the same phenanthrenoid compound (XI).

Route III: By this route, which has no relationship to the two earlier routes, a hydrophenanthrenoid ketone (XXVI or XXVII) was obtained by condensing methylacetyl*cyclo*hexene (XXIII) with *O*-methyl*cyclo*hexanone (XXIV) following the method of Huber as employed in a different preparation (*Ber.*, 1938, **71**, 725). In this reaction, presumably an open-chain unsaturated ketone (XXV) was formed as an intermediate product.



(XXIII) (XXIV) (XXV)

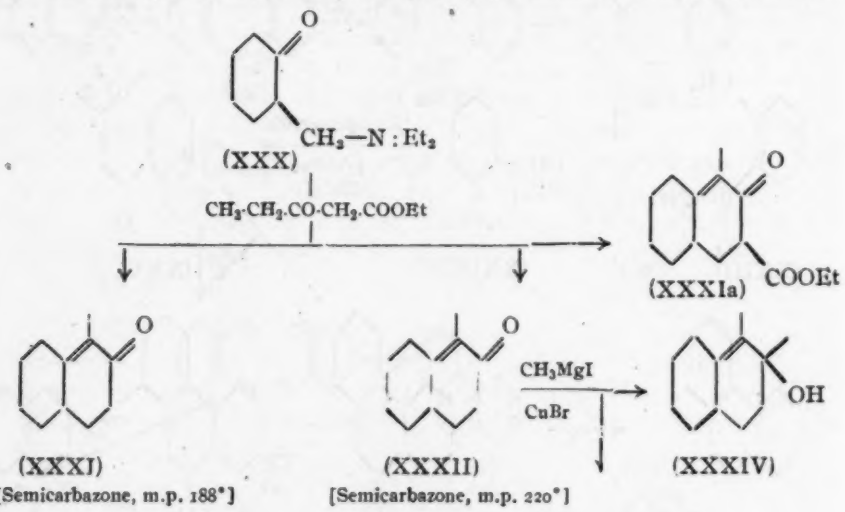
(XXVIII) (XXVI) (XXVII) (XXIX)

It showed the typical absorption spectra of an $\alpha\beta$-unsaturated ketone, which confirmed its cyclic structure. For various reasons, the confirmation of one of the structures by conversion into phenanthrene (XXVIII) or methylphenanthrene (XXIX) through dehydrogenation has not been carried out so far.

Miscellanious approaches: Apart from the routes mentioned above, a few other interesting approaches were also made, though the results were not always positive. Unsuccessful attempts were made to prepare the diketone (VIII) by condensing ethylene dibromide in one or two stages with *cyclo*hexanone or *cyclo*hexanone carboxylic ester in presence of sodium ethoxide or sodamide (Haller and Cornubert, *Compt. rend.*, 1913, **156**, 1199) as employed in other preparations, but instead, only

*cyclo*hexylidene*cyclo*hexanone was obtained. In another experiment, β-*cyclo*hexanonyl alcohol was obtained by hydrolysing the condensation product of *cyclo*hexanone carboxylic ester with β-chloroethylacetate, but in view of the unsatisfactory yield, it was not further processed to (VIII).

Finally, in another interesting series of experiments methoiodide of the Mannich base (XXX), obtained from *cyclo*hexanone (*Ber.*, 1937, **70**, 355), was condensed with β-ketovaleric ester (Robinson, *J. Chem. Soc.*, 1937, 53) to produce a mixture of two isomeric, hitherto unknown, αβ-unstaturated ketones, 2-keto-1-methyl-$\Delta^{1:9}$-octalenes (XXXI and XXXII), which could be separated through their semicarbazones or through their differential reactivity towards magnesiummethyl iodide, as the keto group present in one of these was quite resistant towards Grignard's reagent. In next stage, attempt was made to prepare the dimethyldecalone derivative (XXXIII) *via* the method of β-alkylation in presence of magnesiummethyl iodide and cuprous bromide (Birch and Robinson, *ibid.*, 1943, 501). This was to be converted in subsequent stages into a suitable phenanthrenoid derivative, but instead of the desired compound (XXXIII), the tertiary alcohol, (XXXIV), was obtained as the sole product.



EXPERIMENTAL

2 : 2'-*Dimethoxybenzoin* (IV) was prepared from *o*-methoxybenzaldehyde according to the method of Irvine (*loc. cit.*), and crystallised from a large volume of ether, m.p. 101°.

2 : 2′-*Dimethoxy*-1 : 2-*diphenylethane* (V).—The dimethoxybenzoin (35 g.) was reduced by refluxing with mechanical stirring in a three-necked flask with zinc-amalgam (100 g.) and HCl (conc., 400 c.c., 1 : 1), a slow current of HCl being passed through the reaction mixture. The reaction lasted for about 12 hours when most of the amalgam had gone into solution. After cooling, the reduction product was extracted with ether, washed, dried (Na_2SO_4) and after removal of the solvent it was crystallised from ether-petroleum ether. A second crop was obtained by distilling the mother-liquor (160°-180°/3 mm.) followed by crystallisation; total yield 27.5 g., m.p. 84° (Irvine, *loc. cit.*, records m p. 83-84°).

Working on a small scale (1 g.), it was found that the reduction could be carried out catalytically (PtO_2-EtOH) and crystallising the product in the usual way, m.p. 84°, yield 0.5 g.

2 : 2′-*Dihydroxy*-1 : 2-*diphenylethane* (VI).—The above compound (V: 16 g.) and anhydrous pyridine hydrochloride (40 g.) were heated at 180°-200° for 3 hours with mechanical stirring in a two necked flask fitted with a condenser and a guard tube. The contents after cooling were diluted with water (200 c.c.) when the dihydroxy compound separated as a sticky gum. The gum was dissolved in a known amount of NaOH solution, filtered, and then slowly poured into boiling water (2.5 litres) containing requisite amount of HCl to make the total mixture slightly acidic. It was boiled for 5 to 10 minutes (charcoal, 5 g.) and filtered hot. On keeping overnight the dihydroxy compound separated in the form of fine needles. It was collected by filtration and washed with a little cold water. The mother-liquor on concentration and cooling furnished a second crop of crystals; total yield 10-11 g. A small sample was recyrstallised from hot water, m.p. 114° (Thiele, *Annalen*, 1899, **305**, 97, records m.p. 115°). Crystallisation could also be carried out from dilute alcohol.

Preparation of (VI) *from* o-*Nitrotoluene*.—2:2′-Dinitro-1:2-diphenylethane (XIV) was prepared according to Lapworth (*loc. cit.*). NaOEt (anhyd., 54 g.), *o*-nitrotoluene (137 g.) and ethyl formate (74 g.) afforded the crystalline dinitro compound (23 g.), m.p. 121° (Lapworth, m.p. 121°). On catalytic hydrogenation (Raney nickel, 100°, 100 atmosphere) it was quantitatively reduced to the diamino compound (XV), m.p. 75° (Durland and Adkins, *loc. cit.*, record m.p. 75°); acetate, m.p. 249° (Thiele, *loc. cit.*, m.p. 249-50°). The diamino compound (5 g.) was then dissolved in HCl (400 c.c. of water and 6 c.c. of conc. acid) and diazotised in the usual way with ice-cooling with addition of sodium nitrite (4 g.), dissolved in a little water. The reaction mixture was then slowly warmed and finally boiled for 15 minutes. Any hydrocarbon formed was removed by a powerful jet of steam. The aqueous solution on cooling deposited crystals of (VI), m.p. 114°, yield 3 g.

2 : 2′-*Dihydroxy*-1 : 2-*dicyclohexylethane* (VII).—The diphenolic compound (VI: 23 g.) on catalytic hydrogenation (150°, 100 atmospheres) in presence of Raney nickel in methanolic solution for 10 hours furnished a quantitative yield (24 g.) of (VII) as a viscous mass which could be crystallised from dilute alcohol, m.p. 139°. (Found: C, 74.28; H, 11.7. $C_{14}H_{26}O_2$ requires C, 74.28; H, 11.6 per cent).

2 : 2'-Diketo-1 : 2-dicyclohexylethane (VIII).—The above diol (20 g.) in glacial acetic acid (100 c.c.) was oxidised by gradual addition of chromic acid (13.3 g. CrO_3, water 20 c.c., glacial acetic acid 60 c.c.) under cooling. The mixture was left at room temperature for 20 minutes and then warmed on the water-bath for another 20 minutes. After addition of water (300 c.c.), the diketo compound was extracted with ether, washed with bicarbonate, water and then dried. The diketo compound (19 g.), left after removal of the solvent, was as such sufficiently pure, but it was further purified by converting it into the disemicarbazone with semicarbazide hydrochloride (25 g.), sodium acetate (40 g.) and requisite amounts of water and alcohol. The yield of the semicarbazone was very satisfactory (25 g.), m.p. 212°. Due to its extremely insoluble nature it was very difficult to crystallise it from alcohol and it therefore showed a little low nitrogen content. (Found: C, 56.9; H, 8.2; N, 23.1. $C_{16}H_{28}O_2N_6$ requires C, 57.1; H, 8.4; N, 25.0 per cent). However, as further purification was not necessary for the next step, it was not attempted. For isolation of the pure diketone, the semicarbazone (25 g.) was heated on the water-bath for 20 minutes with *N*-HCl (400 c.c.) and the liberated diketone extracted with ether and worked up in the usual way. It was crystallised from alcohol, m.p. 84°. The substance sublimed easily. (Found in a sample dried at 50°/2 mm. for 2 hours: C, 75.9; H, 9.6. $C_{14}H_{22}O_2$ requires C, 75.6; H, 9.9 per cent).

2 : 2'-Dihydroxy-2 : 2'-dimethyl-1 : 2-dicyclohexylethane (IX).—To the Grignard solution, prepared from methyl iodide (22 g.), magnesium (4 g.) and ether (150 c.c.), a solution of the above diketone (obtained by decomposition of the semicarbazone, 24 g., and employed as such without crystallisation) in ether (100 c.c.) was added with mechanical stirring (stirring continued for 10 hours) after which the mixture was heated on the water-bath for another 3 hours and then left at room temperature for a further period of 48 hours. After decomposition of the Grignard complex with ammonium chloride and dilute HCl, the ditertiary alcohol was extracted with ether, washed with 2*N*-thiosulphate, water and dried. The yield of the diol after removal of the solvent was quantitative. It could be crystallised from dilute acetone or alcohol, m.p. 114° (unsharp). (Found in a sample dried at 80°/1-2 mm: C, 75.4; H, 11.8. $C_{16}H_{30}O_2$ requires C, 75.53; H, 11.9 per cent).

11 : 12-Dimethyl-$\Delta^{3:4}$-dodecahydrophenanthrene (XI).—The above ditertiary alcohol (13 g.) was mixed with syrupy phosphoric acid (100 c.c., *d* 1.75) and heated at 150°-170° with mechanical stirring for 2 to 3 hours. The mixture after cooling and dilution with water was extracted thoroughly with benzene, washed with bicarbonate, water and dried. The residual oil left after removal of the solvent distilled at 105°-110°/0.8 mm. For purification it was heated over sodium (5 g.) at 180° under slightly reduced pressure for several hours and distilled; it was finally distilled twice over fresh sodium, b.p. 108°/0.5–0.8 mm., yield 7 g. (viscous oil); n_D^{15}, 1.5236. (Found: C, 88.0; H, 12.01. $C_{16}H_{26}$ requires C, 88.0; H, 12.0 per cent).

Catalytic Hydrogenation.—The hydrocarbon (1.0522 g.) in methanol (150 c.c., containing 0.1 c.c. of conc. HCl.) in presence of Adam's platinum oxide catalyst (0.102 g.) on complete hydrogenation (4 hours) absorbed 103.4 c.c. of hydrogen; $C_{16}H_{26}$ √ 1 requires 108.2 c.c.

Dehydrogenation and Isolation of Phenanthrene.—The hydrophenathrene (4 g.) with selenium (8 g.) was heated in a metal bath (350°-400°) for 48 hours. The dehydrogenation product was isolated by extraction of the powdered reaction mixture and the flask with ether in the usual way; the ether was removed and the residue distilled from a micro-retort; yield 2.3 g., b.p. 120°/ (bath temp.) 10^{-4} mm. A part of the distillate on three crystallisations from alcohol furnished pure phenanthrene, m.p. 99-100° (mixed m.p.). Another part was converted into the picrate which was crystallised three times from methanol, m.p. 144° (mixed m.p.).

2-*Keto*cyclo*hexyl carbinol* (XVII) was prepared according to the method of Bodendorf (*loc. cit.*) using barium hydroxide as the condensing agent. *cyclo*-Hexanone (55 g.) and formalin (33 c.c.) afforded the carbinol (14 g.), b.p. 107°/10 mm. The acetate (XVIII) was prepared by acetylating the above carbinol (10 g.) with pyridine (20 g.) and acetic anhydride (10 g.) in the usual way at room temperature; yield 10 g., b.p. 134°/15 mm.

2-*Hydroxy*-2-*methyl*cyclo*hexyl carbinol acetate* (XIX) was prepared by dropwise addition of the Grignard solution, prepared from methyl iodide (52 g.), magnesium (9.4 g.) and ether (200 c.c.) in the conventional way at 0°, to a solution of the acetoxy compound (XVIII: 55 g.) in ether (400 c.c.) with mechanical stirring; stirring was continued for another 3 hours at 0°, and for 48 hours at room temperature. The Grignard complex was decomposed with ammonium chloride and HCl and the product (XIX) after isolation with ether was purified by distillation through a small column; yield 47 g., b.p. 92-95°/1 mm. (Found: C, 64.5; H, 9.5. $C_{10}H_{18}O_3$ requires C, 64.5; H, 9.74 per cent).

2-*Methyl*-Δ^1-cyclo*hexenyl Carbinol* (XXI).—Phosphorus pentoxide (20 g.) was gradually added with mechanical stirring at room temperature to a solution of the acetate (XIX: 31 g.) in dry benzene (400 c.c.) contained in a three-necked flask fitted with a reflux condenser and guard tube. Stirring was continued for 5 hours, after which the reaction mixture was heated on the water-bath for another hour. The benzene solution was then removed by decantation, and the phosphoric acid residue washed with fresh benzene. The combined benzene extract was washed, dried and worked up in the usual way. The residual oil after removal of the benzene was dissolved in methanolic potash (250 c.c., 5%) and refluxed for 30 minutes. After partial removal of the solvent and dilution with water and subsequent extraction with ether, 2-methyl-*cyclo*hexenyl carbinol was isolated by distillation; yield 13 g., b.p. 73-76°/1 mm., n_D^{18} 1.4933. (Found: C, 76.3; H, 10.8. $C_8H_{14}O$ requires C, 76.1; H, 11.1 per cent). It showed colour reaction with tetranitromethane, indicating the presence of unsaturation. The substance (0.254 g.) in presence of platinum oxide (0.008 g.) in methanol (50 c.c.) on complete hydrogenation absorbed 41 c.c. of hydrogen; calc. for $C_8H_{14}O$ $\sqrt{1} = 44.9$ c.c.

1-*Methyl*-Δ^2-cyclo*hexenylmethyl Bromide* (XXII).—The above carbinol (20 g.) was dissolved in dry benzene (200 c.c.) and anhydrous pyridine (20 c.c.) in a three-necked flask. PBr_3 (20 g.) was then added dropwise at 0° with mechanical stirring. The mixture was left at room temperature for 48 hours by which time it had developed a light brown colour. After heating for another 1 hour on the water-

bath it was decomposed with ice, further acidified with HCl and the bromide taken up in ether and isolated in the usual way; b.p. 67-70°/1 mm., yield 16 g. It was not analytically pure, as a small amount of the parent alcohol was retained as an impurity. However, as this did not interfere with the ultimate objective, further purification was not attempted.

11:12-*Dimethyl*-$\Delta^{3:4}$-*dodecahydrophenanthrene* (XI).—The contents of three-necked flask fitted with mechanical stirring and containing clean sodium (10 g.) and dry toluene (20 c.c.) were boiled in an oil-bath. The impure bromide (13 g.) was carefully added from a dropping funnel during 5 minutes and the boiling and stirring continued for another 30 minutes. After cooling, the toluene solution of the diene was removed by decantation; the residue in the flask was washed two or three times with fresh toluene, the combined extract filtered, the solvent removed under reduced pressure and the diene collected by fractionation through a small column; b.p. 100°-115°/1 mm., yield 7.1 g. (any unchanged alcohol present in the bromide was eliminated at this stage as the sodio derivative. The formation of any ether by interaction of the bromide and the sodio derivative was not very pronounced as indicated by the ultimate purity of the desired phenanthrenoid). The entire amount of the diene, without further purification, was then cyclised by heating with mechanical stirring for 2 to 3 hours at 150°-160° with syrupy phosphoric acid (60 c.c., *d* 1.75). The hydrophenanthrene compound was then isolated as on the previous occasion and purified by repeated distillation over sodium, yield 2.9 g., b.p. 108-111°/1 mm., viscous oil, n_D^{12}, 1.5253. It was identical in all respects with the product obtained through route I. (Found: C, 87.61; H, 11.74. $C_{16}H_{26}$ requires C, 88.0; H, 12.0 per cent). The hydrophenanthrene (0.500 g.) in presence of platinum oxide (61 mg.) in methanol (70 c.c.) absorbed 51 c.c. of hydrogen; calc. for $C_{16}H_{26}$ $\sqrt{1}$ = 53.5 c.c. This indicated that the cyclisation was complete. The structure of the cyclised product was further confirmed by dehydrogenation with selenium and isolation of phenanthrene, m.p. 100°; picrate, m.p. 144° and mixed m.p.

1-*Methyl*-2-*acetyl*-Δ^1-cyclo*hexene* (XXIII).—Methyl*cyclo*hexene was prepared by dehydration of *O*-methyl*cyclo*hexanol with phosphoric acid and purified by fractional distillation, b.p. 105-108°. Methyl*cyclo*hexene (76 g.) and acetyl chloride (50 g.) in presence of stannic chloride in CS_2 furnished methylacetyl*cyclo*hexene (35 g.), b.p. 80°-90°/11 mm.

Preparation of (XXVI) *or* (XXVII).—Potassium *iso*propoxide, prepared from molecular potassium (12 g.) and *iso*propyl alcohol (63 c.c.), was taken in a three-necked flask fitted with condenser, mechanical stirrer, guard tube and covered with anhydrous pyridine (120 c.c.). A mixture of *O*-methyl*cyclo*hexanone (24 g.) and methylacetyl*cyclo*hexene (30 g.) was slowly added with stirring. The mixture, which after leaving at room temperature for 24 hours had developed a light red colour, was heated on the water-bath for 6 to 7 hours, cooled, diluted with water, acidified with dilute H_2SO_4 and extracted with ether. The extract after usual processing by washing with dilute H_2SO_4, bicarbonate, etc. was carefully fractionated through a small column. The phenanthrenoid compound distilled at 160°-175° (mostly at 170°/1 mm)., yield 9 g. It was a viscous material and did not form any semi-

carbazone. (Found: C, 82.0; H, 10.3. $C_{16}H_{24}O$ requires C, 82.7; H, 10.4 per cent). Slight discrepancy in carbon was probably due to a trace of impurity, removal of which was not attempted for fear of loss. Light alsorption in alcohol (0.0002101 *M*): λ_{max} 239 mμ (log ϵ, 3.77), typical of an $\alpha\beta$-unsaturated ketone.

β-Ketovaleric ester was prepared according to the method of Cook and Robinson (*J. Chem. Soc.*, 1941, 391) from ethylmagnesium iodide and ethyl cyanoacetate and decomposition of the reaction product in the usual way. Ethyl iodide (250 g.) and ethyl cyanoacetate (70 g.) yielded the keto-ester (50-55 g.), b.p. 78°/11 mm.

Mannich Base (XXX).—The bases were prepared by following the original method of Mannich (*loc. cit.*) which was much superior to that of Robinson (*loc. cit.*).

2-Keto-1-methyl-$\Delta^{1:9}$-octalene (XXXI & XXXII).—The methoiodide obtained from the Mannich base (30 g.) in alcohol (100 c.c.) was mixed with the sodio derivative of β-ketovaleric ester, obtained from the ester (30 g.), absolute alcohol (210 c.c.) and sodium (4.8 g.), and refluxed on the water-bath for 7 hours. After removal of the solvent under reduced pressure, the residue was taken up in ether, washed successively with dilute HCl, water and dried and the contents fractionated, using a small column. The crude keto-octalene distilled at 90°-100°/0.5 mm., yield 10 g. A minor higher boiling fraction, b.p. 100°-150°/0.5 mm. (4 g), which was composed of the β-keto ester (XXXIa), also furnshed a little more of the keto-octalene on alkaline hydrolysis. The material was purified through its semicarbazone. The crude ketone (15 g.) produced from alcohol pure (plates) semicarbazone (15.5 g.), m.p. 220°. (Found: C, 65.6; H, 8.62; N, 19.67. $C_{12}H_{19}ON_3$ requires C, 65.2; H, 8.66; N, 19.0 per cent). Light absorption in alcohol (0.0000117 *M*): λ_{max}, 271 mμ (log ϵ, 4.16). The mother-liquor was preserved for the isolation of the semicarbazone of (XXXI).

For the isolation of the pure (XXXII), the semicarbazone was decomposed in the usual way by heating with *N*-H_2SO_4 for 10 to 15 minutes on the water-bath and the liberated ketone isolated and worked up; b.p. 110°-12°/3 mm., viscous oil with a camphor-like odour, yield 9 g., n_D^{17} 1.5326. (Found: C, 80.1; H, 9.96. $C_{11}H_{16}O$ requires C, 80.44; H, 9.82 per cent). Light absorption in alcohol (0.0000757 *M*): λ_{max} 246 mμ (log ϵ, 4.16).

The mother-liquor, left after separation of the first semicarbazone, on concentration and cooling furnished the semicarbazone of (XXXI) which on recrystallisation melted at 188°. (Found: C, 65.0; H, 8.9; N, 18.9. $C_{12}H_{19}ON_3$ requires C, 65.2; H, 8.66; N, 18.9 per cent). This semicarbazone can be better isolated by subjecting the keto-octalene mixture to treatment with MgMeI which preferentially reacted with (XXXII). The reaction product on treatment with semicarbazide hydrochloride furnished the semicarbazone of (XXXI) which had remained unattacked (0.8 g. of pure semicarbazone from 5.0 g. of the ketone). The free ketone was obtained as in the previous case by decomposition with H_2SO_4; b.p. 70-72°/0.1 mm.

(Found : C, 79.90 ; H, 10.22. $C_{11}H_{16}O$ requires C, 80.44 ; H, 9.82 per cent). $\lambda_{max.}$ (alcohol), 248 mμ (log ϵ, 3.94).

The author expresses his deep gratitude to Dr. B. Lythgoe and Prof. A.R. Todd of the University of Cambridge where the work was carried out.

NATIONAL CHEMICAL LABORATORY OF INDIA,
POONA-8.

Received October 21, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 8, 1956]

REDUCTION OF COPPER BORATE BY HYDROGEN

By S. K. Deb and M. H. Khundkar

Reduction of crystalline copper borate, $CuO.B_2O_3$, by hydrogen follows the course : $CuO.B_2O_3 + H_2 = Cu + B_2O_3 + H_2O$. In the temperature range of 500° to 750°, the reduction is fairly rapid and goes to completion in about 30 minutes at 750°. The reduction process is probably accompanied with the phenomenon of activated adsorption.

Copper oxide is known to be easily reduced by carbon. Tammann and Zvoruikin (*Z. anorg. allg. Chem.*, 1928, **170**, 62) found 700° and 790° as starting points in the reduction of cupric oxide by sugar charcoal and graphite respectively. Khundkar (this *Journal*, 1952, **29**, 467) studied the reduction of copper oxide by carbon in presence of B_2O_3 and $Na_2B_4O_7$ melts in the temperature range of 600°-750°, in which these melts themselves were inert towards carbon. It was observed that in the absence of carbon, copper oxide combined with B_2O_3 to form a borate (a new, but unidentified X-ray diffraction pattern), which was later reduced by carbon to metallic copper, through the intermediate formation of Cu_2O. In continuation of that work, we report here a study of the reduction of pure crystalline copper borate by hydrogen.

Experimental

The crystalline copper borate was prepared by heating an intimate mixture of CuS and $Na_2B_4O_7$ (in the molar ratio of 1 : 1) in a platinum crucible at 900° for about 2 hours in presence of air. Blue, needle-shaped crystals of copper borate, so obtained, was purified from the reaction product by treatment with HCl (conc.) in which the crystalline borate remained insoluble. It was finally washed thoroughly with water and dried. On determination of copper and borate (Haider and Rahim, *Pakistan J. Sci. Res.*, 1952, **4**, 65) it was found to conform to the composition, $CuO.B_2O_3$. (Found : Cu, 42.25, 42.90; B, 14.45, 14.45. Calc. for $CuO.B_2O_3$: Cu, 42.60; B, 14.50 per cent).

The apparatus used for studying the reduction was more or less the same as that described by Khundkar (this *Journal*, 1952, **29**, 341) but the right hand side of the main system was connected to a gas circulating pump instead of the CO-CO_2 determination train. By this set up, it was possible to start the reaction in an atmosphere of hydrogen and follow the progress of reduction from the decrease in gas volume at different intervals of time. The water vapour formed during the reaction was absorbed in P_2O_5, taken in a boat and placed in the exit (cooler) end of the reaction tube. The gas circulating system ensured uniform circulartion of gas throughout the entire reaction system. Reactions were carried out in a small platinum boat.

Analysis of the Product.—Interpretation of the results was based on the analysis of the solid products of reaction. The procedure of analysis is schematically outlined below :

$CuO.B_2O_3$

↓ Reduction

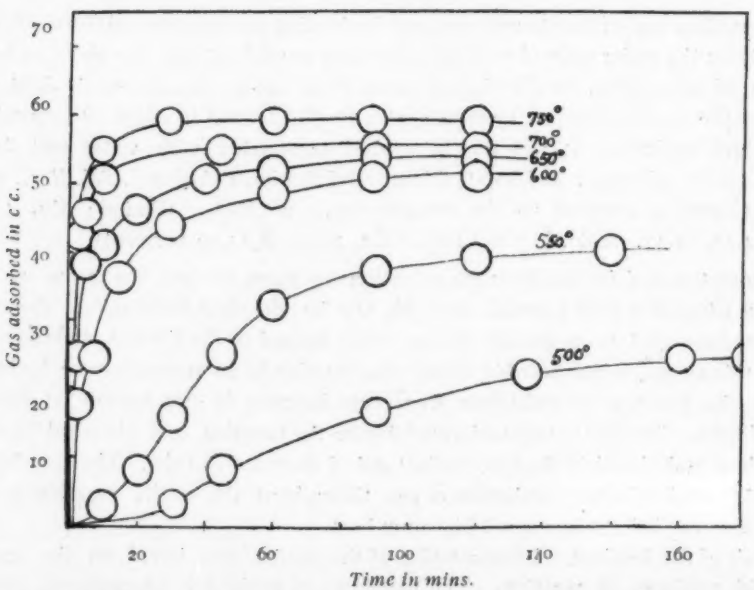
Solid products

↓ Extraction with hot water

Hot water extract (free boric acid determined).	Residue ↓ Treated with hot nitric acid
	Solution (total copper determined according to standard procedure). / Residue (unchanged crystalline copper borate).

Separate experiments were carried out at different temperatures in the range 500° to 750°. In order to compare the results better, the same amount of reactant (viz. 0.25 g.) was taken in each case. The total volumes of gas adsorbed (corrected to N.T.P.) at different intervals of time have been plotted in Fig. 1. At 600° the adsorption of hydrogen has a short induction period. Between 500° and 700°, the decrease in the volume of hydrogen is extremely rapid during the first ten minutes. After this, the adsorption (reduction) proceeds very slowly and comes to a steady state in about two hour's time.

FIG. 1



The theoretical amount of hydrogen required for complete reduction to copper (without affecting the B_2O_3) is 37.5 c.c. It is thus clear that either the B_2O_3 has been

partially reduced or the reduction process is associated with adsorption of gas in excess of that required for reduction. The free energy of formation of B_2O_3 ($-\Delta G$) is considerably high; and also from available literature, it appears improbable that B_2O_3 will be reduced to boron at such low temperatures. The question of adsorption will be discussed in a later section.

Extent of Reduction at different Temperatures.—It was observed that in the products of reduction there was, at all temperatures, an amount of free boric oxide that could be extracted with water. It seems probable that the borate is reduced to metallic copper and boric oxide is released. A similar reaction was observed in the case of zinc silicate reduction by Kitchener and Ignatowicz (*Trans. Faraday Soc.*, 1951, **47**, 1278):

$$Zn_2SiO_4 + 2H_2 = 2Zn + 2H_2O + SiO_2.$$

In the case of copper borate, however, the reduction may proceed directly as in (*i*) or through the intermediate formation of a cuprous borate, as in (*ii*) below:

$$CuO.B_2O_3 + H_2 = Cu + B_2O_3 + H_2O \quad \ldots \quad \ldots \quad (i)$$

$$\left.\begin{aligned} 2\,CuO.B_2O_3 + H_2 &= Cu_2O.2B_2O_3 + H_2O \\ Cu_2O.2B_2O_3 + H_2 &= 2Cu + 2B_2O_3 + H_2O \end{aligned}\right\} \quad \ldots \quad \ldots \quad (ii)$$

Existence of a yellow cuprous borate has been mentioned (Mellor, "Comprehensive Treatise in Inorganic and Theoretical Chemistry", Vol. V, p. 84, Longmans, 1924), but, nothing is known definitely about its composition or properties. If the cuprous borate is insoluble in strong nitric acid, it would contaminate the final residue (vide scheme of analysis); but in all cases it has been found that the unchanged residue after treatment with nitric acid is a perfectly blue crystalline mass (except for reaction at 750°, where nothing is left behind). It is probable that the cuprous borate could have been soluble in strong acid and thus extracted with metallic copper. But in such extracts, no test for boric acid was found, indicating that there was no intermediate formation of cuprous borate as a stable phase. A final evidence is to be obtained from results in Table I.

TABLE I

Analysis of products of reduction of copper borate by hydrogen at different temperatures.

$CuO.B_2O_3$ taken = 0.25 g. (corresponds to 0.1065 g. Cu and 0.1168 g. B_2O_3).

Temp.	Reduction Period.	B_2O_3 in water extract.		Cu in acid extract.		Mean value of reduction.
500°	180 mins.	0.0760 g.	65.1 %	0.0693 g.	65.1 g.	65.1 %
550°	120	0.0853	73.0	0.0777	73.0	73.0
600°	90	0.0971	83.1	0.0900	84.5	83.8
650°	90	0.1015	86.9	0.0927	87.1	87.0
700°	45	0.1075	92.0	0.1007	94.6	93.3
750°	30	0.1150	98.5	0.1064	99.9	99.2

The amount of free boric acid was determined in the product of each experiment and expressed in terms of percentage of total B_2O_3 input (as copper borate). Also the copper obtained in the acid extract was expressed in terms of percentage of total copper input. A close resemblance of the two sets of results also indicates that the reduction

proceeds directly to the formation of metallic copper according to equation (*i*), above. The mean of the two values has been taken as the extent of reduction at a particular temperature. The period of reduction was not, however, the same in each case. Instead. at each temperature, the reduction was continued till it was so slow that not more than 1.0 c.c. of hydrogen was adsorbed in one hour. At 500°, the reduction is fairly high, 65.1%. It increases steadily with increase of temperature. The progress of reaction (percentage reduction) can be represented by the reaction,

$$Y = 0.1364\ t - 3.1,$$

where Y is the percentage conversion to metallic copper, and t is the temperature in degrees centigrade.

Phenomenon of Adsorption.—In Table II, a set of results is presented (column 3) for the theoretical amounts of hydrogen required for reduction, as calculated from the mean value of the extent of reduction. This has been compared with the actual values of hydrogen adsorbed (obtained from the curves in Fig. 1).

TABLE II

Adsorption of hydrogen at different temperatures in the reduction of copper borate. $CuO.B_2O_3$ in each experiment = 0.25 g.

Temp.	Reduction Mean value.	* Vol. of H_2 reacted.	Actual vol. (total) of H_2 adsorbed.	Vol. of H_2 adsorbed in excess.
500°	65.1 %	24.5 c.c.	24.2 c.c.	− 0.3 c.c.
550°	73.0	27.4	39.2	+11.8
600°	83.8	31.3	51.2	+19.9
650°	87.0	32.7	53 5	+20.8
700°	93.3	35.0	54.6	+19.6
750°	99.2	37.2	59.0	+21.8

* As computed from column 2.

At 500°, there is no excess of hydrogen adsorbed over that required for reduction. The difference between the total hydrogen adsorbed and that reacted (called excess hydrogen) increases with increase of temperature and appears to reach a limiting value. The adsorption resembles the "activated adsorption" observed in the case of manganese and chromic oxides by Taylor *et al.* (*J. Amer. Chem. Soc.*, 1931, **53**, 2168). But a fundamental difference is that the present case is complicated by the simultaneous reduction of borate. The limiting value of the excess hydrogen adsorbed (600°-750°) can be taken to be approximately 20 c.c., corresponding to 0.88 mg. mole (or 1.76 mg. atom). The amount of $CuO.B_2O_3$ taken (0.25 g.) was 1.68 mg. mole. It thus appears that the adsorption probably tends to a saturation value of one atom of hydrogen for each molecule of $CuO.B_2O_3$ taken or B_2O_3 formed.

The idea of activated adsorption is not, however, conclusively established. Because there is a possibility that some hydrogen might have been consumed in the reduction of B_2O_3 to some unstable suboxides of boron, formation of which (or otherwise) could not be definitely proved.

DEPARTMENT OF CHEMISTRY,
DACCA UNIVERSITY,
EAST PAKISTAN.

Received February 28, 1956.

[Jour. Indian Chem. Soc., Vol. 33, No. 8, 1956]

STUDIES IN VAT DYES. PART V. THE ACYL DERIVATIVES OF MONO- AND DI-AMINOANTHRAQUINONES USING LONG-CHAIN FATTY ACIDS

By R. D. Desai and R. N. Desai

Lauryl, palmityl and stearyl derivatives of 1-amino-, 2-amino-, 1:4-diamino-, 1:5-diamino- and 2:6-diaminoanthraquinones have been prepared. These amidoanthraquinones are useless as vat dyes owing to their inability to vat, but are soluble in vegetable oils.

Among the anthraquinone vat days, the acylamidoanthraquinones are notable for their simplicity of structure and the method of preparation. The aminoanthraquinones are capable of vatting, but the alkali salts of the "leuco" compounds have no affinity for cotton. Deinet (*J. Soc. Dyers & Col.*, 1914, **30**, 29) observed that benzoylation of 1-aminoanthraquinones had the remarkable effect of transforming them into vat dyes, with adequate affinity for practical dyeing. It is an important fact that one or more of the acylamido groups must be in the α-position of the anthraquinone nucleus. While α-benzamidoanthraquinone is a yellow vat dye (Algol yellow WG; CI, 1126; Bayer & Co., E.P. 270209; U.S.P. 957041; G.P. 216772, 225232), the β-isomer is devoid of any dyeing property. The simple monobasic, as well as dibasic, aliphatic and aromatic acids have been used for acylation, but long-chain fatty acids have not been used. We therefore thought of preparing this type of compounds by condensing acid chlorides of long-chain fatty acids, viz. lauric acid, palmitic acid and stearic acid, with various mono- and di-aminoanthraquinones, viz. 1-aminoanthraquinone, 2-aminoanthraquinone, 1:4-diaminoanthraquinone, 1:5-diaminoanthraquinone and 2:6-diaminoanthraquinone. The acylation has been carried out by condensing previously prepared acid chlorides with the various aminoanthraquinones in presence of dry nitrobenzene.

In the case of diaminoanthraquinones, one acyl group reacted with only one amino group. The structures of these compounds have been proved by preparing their acetyl derivatives, whereby their free amino groups reacted with acetic anhydride, forming the acetylamido-acylamidoanthraquinones. The compounds so formed are highly coloured, varying from golden yellow to brick-red, but owing to their inability to vat, they are useless as vat dyes. However, they are soluble in vegetable oils.

Experimental

The acid chlorides were prepared using thionyl chloride at 60°-70° (Beilstein, Vol. **2**, pp. 363, 374, 384).

1-*Stearylamidoanthraquinone* was prepared by condensing 1-aminoanthraquinone (10 g.) with stearyl chloride (13.1 g.) in presence of nitrobenzene (80 c.c.), using an air condenser. It crystallised from chlorobenzene as golden yellow shining needles, m.p. 128°. (Found: N, 2.6. $C_{32}H_{33}O_3N$ requires N, 2.86 per cent).

All other compounds of the series, prepared in a similar manner, are tabulated in Table I.

TABLE I

[A = Anthraquinone. S = Stearylamido-. P = Palmitylamido-. L = Laurylamido-].

Compound.	Form and solvent.	Formula.	M.P.	% Nitrogen Found.	% Nitrogen Calc.
2-S-A.	Lemon-yellow plates from toluene.	$C_{32}H_{43}O_3N$	184°	2.77	2.86
4-Amino-1-S-A.	Dark violet needles from nitrobenzene,	$C_{32}H_{44}O_3N_2$	112°	5 30	5 55
4-Acetylamido-1-S-A.	Reddish violet shining amorphous powder from acetic acid.	$C_{34}H_{46}O_4N_2$	99°	5.00	5.12
5-Amino-1-S-A.	Bright golden yellow needles from benzene.	$C_{32}H_{44}O_3N_2$	120°	5 40	5.55
5-Acetylamido-1-S-A.	Orange amorphous powder from acetic acid.	$C_{34}H_{46}O_4N_2$	143°	5.20	5.12
6-Amino-2-S-A.	Brownish amorphous powder from nitrobenzene.	$C_{32}H_{44}O_3N_2$	272°	5.60	5 55
6-Acetylamido-2-S-A.	Blackish brown powder from acetic acid.	$C_{34}H_{46}O_4N_2$	72°	5.17	5.12
1-P-A.	Bright golden yellow needles from aviation spirit (b.p. 80-120°).	$C_{32}H_{43}O_3N$	129°	2.87	3.00
2-P-A.	Lemon-yellow flakes from xylene.	$C_{32}H_{43}O_3N$	182°	2.78	3 00
4-Amino-1-P-A.	Deep violet needles from toluene.	$C_{30}H_{40}O_3N_2$	115°	5.76	5.88
4-Acetylamido-1-P-A.	Dark violet powder from acetic acid	$C_{32}H_{42}O_4N_2$	122°	5.47	5.40
5-Amino-1-P-A.	Shining golden yellow needles from aviation spirit (b.p. 80-120°).	$C_{30}H_{46}O_3N_2$	123°	5.69	5.88
5-Acetylamido-1-P-A.	Yellowish orange crystals from acetic acid	$C_{32}H_{42}O_4N_2$	168°	5.34	5.40
6-Amino-2-P-A.	Brownish amorphous powder from nitrobenzene.	$C_{30}H_{40}O_3N_2$	280°	6.00	5.88
6-Acetylamido-2-P-A.	Dark brown powder from acetic acid.	$C_{32}H_{42}O_4N_2$	292°	5.30	5.40
1-L-A.	Golden yellow needles from aviation spirit (b.p. 80-120°).	$C_{26}H_{31}O_3N$	128°	3.30	3.45
2-L-A.	Yellow needles from alcohol.	$C_{26}H_{31}O_3N$	188°	3.50	3.45
4-Amino-1-L-A.	Amorphous powder from methyl alcohol.	$C_{26}H_{32}O_2N_2$	114°	6 72	6 60
4-Acetylamido-1-L-A.	Violet powder from acetic acid.	$C_{28}H_{34}O_4N_2$	130°	5.82	6 00
5-Amino 1-L-A.	Microscopic golden yellow needles from aviation spirit (b.p. 80-120°).	$C_{26}H_{32}O_2N_2$	150°	6 50	6.60
5-Acetylamido 1-L-A.	Orange microscopic needles from acetic acid.	$C_{28}H_{34}O_4N_2$	156°	6.10	6.00
6-Amino-2-L-A.	Brownish amorphous powder from aniline.	$C_{26}H_{32}O_2N_2$	287°	6.55	6.60
6-Acetylamido-2-L-A.	Dark brown amorphous powder from acetic acid.	$C_{28}H_{34}O_4N_2$	286°	6.20	6.00

The authors take this opportunity in expressing their grateful thanks to the Governing Body of the Ahmedabad Education Society for the provision of research facilities.

DEPARTMENT OF CHEMISTRY,
L. D. ARTS COLLEGE & M. G. SCIENCE INSTITUTE,
AHMEDABAD-9.

Received February 28, 1956.

[Jour. Indian Chem. Soc., Vol. 33, No. 8, 1956]

STUDIES IN SESQUITERPENES. PART XIII*. SYNTHESIS OF 4:5- AND 4:8-DIMETHYLEUDALENES

By G. S. Krishna Rao and Sukh Dev

To serve as reference compounds, 4:5- and 4:8-dimethyleudalenes have been synthesised and suitably characterised. Incidentally, a simpler preparation of 4-methyleudalene has been achieved.

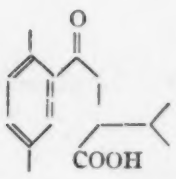
In the study of sesquiterpenoids alkylcadalenes (Campbell and Soffer, *J. Amer. Chem. Soc.*, 1942, **64**, 417; Sukh Dev, this *Journal*, 1948, **25**, 69, 315; Gupta and Muthana, *J. Indian Inst. Sci.*, 1953, **35**, 131, 259, 310) and alkyleudalenes (Ruzicka *et al.*, *Helv. Chim. Acta*, 1933, **16**, 268; Bradfield *et al.*, *J. Chem. Soc.*, 1936, 667, 673, 1137, 1141; 1937, 760, 763; Gupta and Muthana, *J. Indian Inst. Sci.*, 1953, **35**, 263, 307) serve as useful reference compounds. This communication describes the syntheses of 4:8- and 4:5-dimethyleudalenes.

4:8-*Dimethyleudalene* (VI)

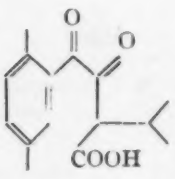
This hydrocarbon has been synthesised by an extension of the succinic anhydride synthesis (Berliner, "Organic Reactions", Vol. 5, 1949, p. 229; Sukh Dev and Guha, this *Journal*, 1948, **25**, 13). The Friedel-Crafts condensation of *iso*propylsuccinic anhydride with *p*-xylene in nitrobenzene solution afforded α-*iso*propyl-β-(2:5-dimethylbenzoyl)-propionic acid (I). In analogy with the reaction of methylsuccinic anhydride with aromatic hydrocarbons (vide Sukh Dev and Guha, *loc. cit.*) and in accordance with the theoretical principles (Desai and Wali, *Proc. Ind. Acad. Sci.*, 1937, **6A**, 135; Wali *et al.*, *ibid.*, 1941, **14A**, 139; Rothstein and Saboor, *J. Chem. Soc.*, 1943, 425) governing these condensations, the product was expected to have the desired structure. However, further evidence in favour of this structure was obtained by its conversion into the diketocarboxylic acid (II) *via* its *iso*nitroso derivative; oxidative cleavage of (II) with alkaline hydrogen peroxide furnished 2:5-dimethylbenzoic acid and *iso*propylmalonic acid.

The Clemmensen reduction of the keto-acid (I) proceeded smoothly to yield α-*iso*propyl-γ-(2:5-dimethylphenyl)-butyric acid (III). The latter on intramolecular acylation with polyphosphoric acid (PPA) afforded the tetralone (IV) in good yield. The ketone was inert to the 2:4-dinitrophenylhydrazine even under forcing conditions (Josten, *Ber.*, 1938, **71**, 2230; Szmant and McGinnis, *J. Amer. Chem. Soc.*, 1950, **72**, 2890; Sonntag *et al.*, *ibid.*, 1953, **75**, 2283).

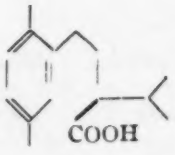
* Part XII. This *Journal*, 1952, **29**, 721.



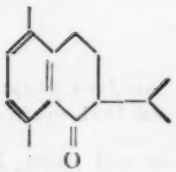
(I)



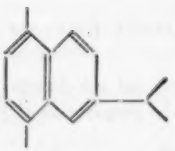
(II)



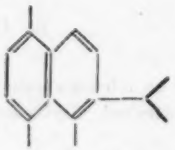
(III)



(IV)



(V)



(VI)

The above ketone on the Clemmensen reduction, followed by sulphur-dehydrogenation, afforded the known 4-methyleudalene (V) (Ruzicka *et al.*, *loc. cit.*); this constituted a far superior synthesis of 4-methyleudalene.

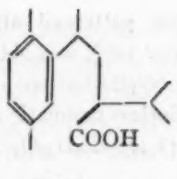
The tetralone (IV) was treated with methyllithium and the crude tertiary alcohol, thus obtained, was dehydrated with formic acid to yield the 5:6-dihydro derivative of (VI). The latter on dehydrogenation with sulphur furnished the required 4:8-dimethyleudalene (VI) (Table I).

4:5-*Dimethyleudalene* (XI)

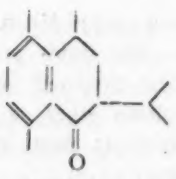
This hydrocarbon was synthesised by two methods, both passing through the ketone (VIII).

*iso*Propylallylacetic acid was condensed with *p*-xylene in the presence of anhydrous aluminium chloride to afford a satisfactory yield of α-*iso*propyl-γ-(2:5-dimethylphenyl)-valeric acid (VII). This was cyclised, in an excellent yield, with PPA to afford the ketone (VIII), which like its analogue (IV) was indifferent to the various carbonyl reagents.

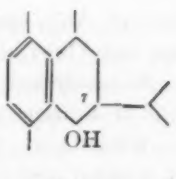
Lithium aluminium hydride reduction of this ketone afforded a mixture of the tetralol (IX) and its dehydration product (X). The great susceptibility of this alcohol to water-elimination is understandable, if we consider the conformation of the tetralol (IX); since the carbonyl group is hindered, the lithium aluminium hydride reduction will chiefly yield the alcohol with the hydroxyl in the quasi-axial position (Barton, *J. Chem. Soc.*, 1953, 1027; Barton *et al.*, *Chem. & Ind.*, 1954, 21) which being anti to the axial-hydrogen on C_7 (the bulkier *iso*propyl group being assigned the stabler equatorial conformation) will undergo a facile elimination; further driving force is provided by the tertiary nature of the C_7-hydrogen and the resultant enhanced conjugation in the hydrocarbon (X).



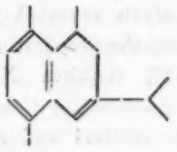
(VII)



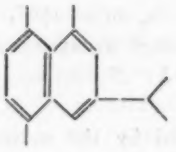
(VIII)



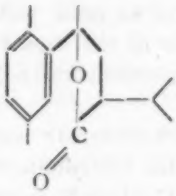
(IX)



(X)



(XI)



(XII)

The crude reduction product of the tetralone (VIII) was completely dehydrated with a trace of iodine and the pure (X) dehydrogenated with sulphur to afford the 4 : 5-dimethyleudalene (XI) (Table I).

The second route utilised the keto-acid (I), described above. The action of methylmagnesium iodide on its methyl ester afforded the lactone (XII). This was converted into the corresponding tetralone (VIII) in a single step, which involved the reductive cyclisation with hydriodic acid and red phosphorus (Sukh Dev, this *Journal*, 1948, **25**, 69, 323). The identity of this preparation of the ketone (VIII) with the product, obtained by the first method, was established by its conversion (sodium-alcohol reduction → dehydrogenation) into the same hydrocarbon (XI).

TABLE I

	M.P. of the dimethyleudalenes.		4-Methyleudalene.
	4:5—.	4:8—.	
Picrate	119·5°	97°	102-103°
Picramide complex	161°	164°	...
Trinitrobenzene ,,	144°	138°	146°
Trinitrotoluene ,,	53°	...	...
Trinitrofluorenone ,,	143°	127-28°	107°

EXPERIMENTAL*

4 : 8-*Dimethyleudalene* (VI)

α-iso*Propyl-β-(2 : 5-dimethylbenzoyl)-propionic Acid* (I).—*p*-Xylene (freshly rectified over sodium; 39 g., 0.368 *M*) was condensed with *iso*propylsuccinic anhydride (Schleicher, *Annalen*, 1892, **267**, 114; 47.3 g., 0.333 *M*) in dry nitrobenzene (520 c.c.)

* All melting and boiling points are uncorrected. Petroleum ether employed was the fraction with b.p. 40°-60°.

in the presence of $AlCl_3$ (anhyd., 100 g., 0.736 *M*) in a manner patterned after that of Sukh Dev and Guha (*loc. cit.*). The crude product, m.p. 106°, was obtained in 69% yield. An analytical sample was prepared by three crystallisations from a mixture (1 : 2) of benzene and petroleum ether as thick colorless prismatic crystals, m.p. 110°. (Found: C, 72.22; H, 8.32; neut. equiv., 247.1. $C_{15}H_{20}O_3$ requires C, 72.58; H, 8.06 per cent. Neut. equiv., 248).

The 2 : 4-*dinitrophenylhydrazone* (HCl method) was purified by two crystallisations from ethanol as thick yellow crystals, m.p. 176°. The analysis revealed that no esterification of the secondary carboxyl group occurred during the preparation of the 2 : 4-dinitrophenylhydrazone. (Found: N, 13.0. $C_{21}H_{24}O_6N_4$ requires N, 13.08 per cent).

The *semicarbazone* was prepared by the sodium acetate method and after two crystallisations from dilute ethanol was obtained as white flakes, m.p. 191°. (Found: N, 14.27. $C_{16}H_{23}O_3N_3$ requires N, 13.8 per cent).

The *amide*, prepared by the addition of liquor ammonia to the acid chloride (PCl_5 method), was crystallised thrice from a mixture of benzene and petroleum ether in colorless needles, m.p. 198.5°. (Found: N, 5.4. $C_{15}H_{21}O_2N$ requires N, 5.67 per cent).

α-iso*Propyl*-β-*oxo*-β-(2 : 5-*dimethylbenzoyl*)-*propionic Acid* (II) *and its Oxidative Cleavage*.—The above keto-acid (2.0 g.) in absolute alcohol (5 c.c.) was added to alcoholic sodium ethoxide (from 0.6 g of sodium and 10 c.c. of ethanol) and amyl nitrite (2 c.c.) introduced with cooling. The mixture was set aside in the frigidaire for 48 hours and diluted with ice water till all the sodium salt went in solution. This was neutralised with dilute sulphuric acid (1 : 1) at 0°, when an oily product separated, which gradually solidified to yield a crude solid (2.1 g.), m.p. 116-20°. The material, which gave a positive test for nitrogen, was used as such for the next step.

The hydrolysis of the above *iso*nitroso derivative was carried out according to a procedure of Barltrop *et al.* (*J. Chem. Soc.*, 1951, 181). A mixture of the above oximinoketo-acid (2.0 g.), aqueous formaldehyde (10 c.c., 40% solution) and 2 *N*-HCl (2 c.c.) was heated on the steam-bath for 20 minutes. On cooling, a white solid (1.1 g., m.p. 114-20°), which developed a deep green colour with ferric chloride solution, separated out; its solution in aqueous sodium hydroxide was yellow. It gave a positive test with periodic acid (Shriner and Fuson, "The Systematic Identification of Organic Compounds", John Wiley, New York, 1940, p.57) and the test for nitrogen was negative.

The above diketo-acid (1.0 g.) was dissolved in aqueous NaOH (5%, 10 c.c.) and H_2O_2 (5%, 10 c.c.) was added. The reaction mixture was heated on the steam-bath for 10 minutes. This was chilled and acidified with HCl (dil.), when a white crystalline solid separated. On recrystallisation from benzene-petroleum ether mixture, it came out as white needles (0.2 g.), m.p. 132°; neut equiv. 149. The 2 : 5-*dimethylbenzoic acid* has m.p. 132° (Heilbron, "Dictionary of Organic Compounds", 1953, p. 284) and neut. equiv. 150.

The filtrate, after separation of the crude 2 : 5-dimethylbenzoic acid, was saturated with sodium chloride and extracted with ether (10 c.c. × 4). After washing with brine (10 c.c. × 2) and drying (Na_2SO_4), the solvent was removed under suction at the laboratory temperature, when an oil was left. This soon solidified and after trituration with a little ice water was collected, m.p. 86-87°, yield 20 mg. This was identified as iso*propylmalonic acid* by a mixed m. p. (Conrad and Bischoff, *Annalen*, 1880, **204**, 145).

α-iso*Propyl*-γ-(2 : 5-*dimethylphenyl*)-*butyric Acid* (III).—The pure keto-acid (12.4 g., 0.05 *M*) was reduced with amalgamated zinc (from zinc wool 40 g., mercuric chloride 4 g., C.P. HCl 2 c.c. and water 60 c.c.) and HCl (C.P., 70 c.c. and water, 30 c.c.) with the addition of toluene (25 c.c.) and glacial acetic acid (1 c.c.) by refluxing for 36 hours. At the end of every six hours HCl (conc., 20 c.c.) was added. The reaction mixture was cooled and the solvent layer was separated. The aqueous portion was extracted with benzene (30 c.c. × 3) and the combined extract washed with brine. The solvents were stripped off and the residue distilled to yield a colorless viscous liquid, b.p. 175-80°/2.5 mm., 198-203°/12 mm., yield 82%. The distillate gradually solidified and crystallised from petroleum ether in thick white prisms, m.p. 77°. (Found : C, 76.2 ; H, 9.13 ; neut. equiv., 232.3. $C_{15}H_{22}O_2$ requires C, 76.9 ; H, 9.4 per cent. Neut. equiv., 234).

From the residue, left after distillation of the crude reduction material, a small quantity (0.5 g.) of the starting keto-acid was recovered. However, the use of alcohol instead of acetic acid during the Clemmensen reduction produced a byproduct (0.4 g.), m.p. 201° (from benzene-petroleum ether mixture) which was insoluble in 30% cold alkali (aq.) ; this was not studied further.

The *amide* crystallised from benzene-petroleum ether mixture in white needles, m.p. 148°. (Found : N, 6.3. $C_{15}H_{23}ON$ requires N, 6.02 per cent).

The *anilide* was obtained as white crystalline material from dilute ethanol, m p. 129-30°. (Found : N, 4.56. $C_{21}H_{27}ON$ requires N, 4.5 per cent).

The S-*benzylthiuronium salt* was crystallised twice from dilute ethanol in white needles, m.p. 139°. (Found : N, 7.01. $C_{23}H_{32}O_2N_2S$ requires N, 6.99 per cent).

2-iso*Propyl*-5 : 8-*dimethyltetralone*-1 (IV).—To PPA (from P_2O_5 50 g., syrupy H_3PO_4 30 c.c., *d* 1.75) at the steam-bath temperature the above butyric acid (9 g.) was added in one lot and was kept at that temperature for one hour with occasional swirling. The product was poured onto ice and extracted with benzene (25 c.c. × 4); the combined extracts were washed with aqueous sodium bicarbonate and then with brine. The solvent was removed after drying (sodium sulphate) and the residue fractionated to yield the tetralone as a colorless liquid, b.p. 141-43°/2 mm., n_D^{28}, 1.5420 ; yield 78%. (Found : C, 82.88 ; H, 9.36. $C_{15}H_{20}O$ requires C, 83.33 ; H, 9.2 per cent). The ketone failed to yield a 2:4-dinitrophenylhydrazone or a semicarbazone.

4-*Methyleudalene* (V).—The above tetralone (3 g.) on the Clemmensen reduction with amalgamated zinc (from zinc wool 8 g.), as described above, afforded the corresponding tetralin, which was on rectification over sodium gave a colorless liquid, b.p. 130°/2 mm., yield 2.4 g.

The hydrocarbon (0.55 g.) was heated with sulphur (0.17 g.) at 220°-230° for 1½ hours under slight suction. The product was taken up in petroleum ether (2 c.c.) and passed down a column of activated alumina (10 g.) which was washed with petroleum ether (30 c.c.). From the petroleum ether washings the solvent was removed and the residue distilled over sodium to yield a material (0.22 g.) with b.p. 117°/1 mm., $n_D^{28°}$ 1.5765.

The *picrate* was obtained in orange-red needles from ethanol, m.p. 102-103° (Ruzicka *et al.*, *loc. cit.*, record m.p. 103°).

The *trinitrobenzene complex* crystallised from ethanol in golden yellow needles, m.p. 146° (Ruzicka *et al.*, *loc. cit.*, record m.p. 145.5°).

The *trinitrofluorenone* addition compound was twice crystallised from 80% acetic acid in orange needles, m.p. 107°.

4:8-*Dimethyleudalene* (VI).—The tetralone (IV: 5 g.) in dry ether (150 c.c.) was added to a solution of methyllithium (from lithium 1 g., methyl iodide 10 c.c., and ether 100 c.c.) under nitrogen atmosphere during ½ hour with swirling and cooling in an ice-salt bath. The reaction mixture was left overnight at room temperature (25°) and then decomposed by the slow addition of dilute HCl (1:1; 50 c.c., 20 minutes) with stirring and external cooling. The ether layer was removed, washed with brine and the solvent flashed off. The crude carbinol, thus obtained as the residue, was heated with formic acid (85%, 50 c.c.) for 3 hours on the steam-bath. This was diluted with water and the product taken up in ether. After washing with brine and drying (Na_2SO_4) the solvent was removed and the residue fractionated over sodium to yield 5:6-*dihydro*-4:8-*dimethyleudalene* as a colorless, mobile liquid, b.p. 123-24°/2 mm., $n_D^{28°}$ 1.5355, $d_D^{28°}$ 0.9493, M_D 70.2 (calc. M_D, 69.84); yield 1.4 g.

This hydrocarbon (1.35 g.) was dehydrogenated by heating with sulphur (0.2 g.) for 1½ hours at 210°-220°. The product was distilled off and the distillate (0.6 g.) was converted into the *trinitrobenzene* (*TNB*) *complex* in alcohol. On four crystallisations from ethanol it separated as golden yellow needles, m.p. 138°, yield 0.95 g. (Found: N, 9.71. $C_{22}H_{23}O_6N_3$ requires N, 9.86 per cent).

The pure 4:8-*dimethyleudalene* (VI) was regenerated from the addition compound by filtration of its benzene solution through a column of activated alumina (15 g.), which was then washed with petroleum ether (50 c.c.). The eluate was stripped off the solvent and the dimethyleudalene rectified over sodium as colorless, mobile liquid, b.p. 130°/1.5 mm., $n_D^{27°}$ 1.5970, yield 90%. (Found: C, 90.2; H, 9.34. $C_{16}H_{20}$ requires C, 90.57; H, 9.43 per cent).

The *picrate* on two crystallisations from ethanol was obtained as red needles, m.p. 97°. (Found: N, 9.52. $C_{22}H_{23}O_7N_3$ requires N, 9.52 per cent).

The *trinitrofluorenone* (*TNF*) *complex* was prepared in the usual manner and crystallised four times from 80% acetic acid to yield deep scarlet-red needles, m.p. 127-28°. (Found: N, 7.98. $C_{29}H_{23}O_7N_3$ requires N, 7.97 per cent).

The *picramide* (*TNA*) *addition compound* was prepared in ethanol and after two recrystallisations from the same solvent was obtained as deep yellow needles, m.p. 164°. (Found: N, 12.2. $C_{22}H_{24}O_6N_4$ requires N, 12.7 per cent).

4 : 5-*Dimethyleudalene* (XI)

α-iso*Propylallylacetic Acid*.—Diethyl allylmalonate (Linstead and Rydon, *J. Chem. Soc.*, 1933, 580) was condensed with *iso*propyl bromide according to the procedure of Hjelt (*Ber.*, 1896, **29**, 1855). The ethyl α-*iso*propylallylmalonate (80 g.), thus obtained, was saponified by stirring and refluxing it with KOH (106 g.) in water (140 c.c.) till the ester layer had disappeared (24-36 hours). Working up in the usual manner yielded the crude malonic acid (58 g., 94%), m.p. 103° ; a sample was recrystallised repeatedly first from benzene-petroleum ether and then from water as white prisms, m.p. 122-23° (Hjelt, *loc. cit.*, reported m.p. 112.5°). (Found : C, 58.06 ; H, 7.58. $C_9H_{14}O_4$ requires C, 58.07 ; H, 7.53 per cent). The malonic acid on decarboxylation at 180° for one hour under slight suction yielded the crude α-*iso*propylallylacetic acid, which was purified by distillation, b.p. 121-22°/20 mm., yield 80%.

The S-*benzylthiuronium salt* was prepared in the usual manner as white glistening flakes (water), m.p. 118°. (Found : N, 9.16. $C_{16}H_{24}O_2N_2S$ requires N, 9.09 per cent).

α-iso*Propyl*-γ-(2 : 5-*dimethylphenyl*)-*valeric Acid* (VII).—To a mixture of *p*-xylene (21 g., 0.2 *M*) and α-*iso*propylallylacetic acid (14.2 g., 0.1 *M*) anhydrous $AlCl_3$ (14 g., 0.105 *M*) was added with stirring at room temperature (no external cooling) during 15 minutes ; the reaction was exothermic. The reaction mixture was gently refluxed for 10 minutes and decomposed by pouring on ice (100 g.) and HCl (20 c.c.). The product was taken up in benzene (25 c.c. × 3), washed with dilute HCl and then separated into acidic and neutral portions by extraction with aqueous sodium bicarbonate. The acidic portion on working up gave the required acid (VII), b.p. 158°-162°/2 mm., yield 11.2 g. (45%). (Found : C, 76.74 ; H, 10.08 ; neut. equiv., 246. $C_{16}H_{24}O_2$ requires C, 77.4 ; H, 9.68 per cent. Neut. equiv., 248). The neutral portion was not examined further.

The *piperazonium salt* of the acid was prepared by the method of Pollard *et al.* (*J. Amer. Chem. Soc.*, 1934, **56**, 1759). After two crystallisations from acetone it was obtained as a white microcrystalline powder, m.p. 164-65°. (Found : N, 8.39. $C_{20}H_{34}O_2N_2$ requires N, 8.38 per cent).

2-iso*Propyl*-4 : 5 : 8-*trimethyltetralone*-1 (VIII) : (*i*) *By PPA Cyclisation of* α-iso-*Propyl*-γ-(2 : 5-*dimethylphenyl*)-*valeric Acid* (VII).—The above acid (10 g.) was cyclised by PPA (from P_2O_5, 60 g. and phosphoric acid, 36 c.c.) in the manner outlined above for 2-*iso*propyl-5 : 8-dimethyltetralone-1 (IV). The ketone was obtained as a colorless, mobile liquid, b.p. 132°/2 mm., n_D^{24} 1.5390, yield 90%. (Found : C, 82.94 ; H, 9.50. $C_{16}H_{22}O$ requires C, 83.48 ; H, 9.57 per cent).

(*ii*) *From* α-iso*Propyl*-β-(2 : 5-*dimethylbenzoyl*)-*propionic Acid* (I).—The keto-acid (I : 6.24 g.) was refluxed for 12 hours with a mixture of dry methanol (12 c.c.), benzene (15 c.c.) and sulphuric acid (C.P., 1.4 c.c.). This was worked up in the usual manner to yield the *methyl ester* as a colorless liquid, b. p. 153-55°/1 mm., n_D^{28} 1.5080, yield 90%. (Found : C, 73.11 ; H, 8.68. $C_{16}H_{22}O_3$ requires C, 73.28 ; H, 8.40 per cent).

To the above ester (5.5 g.) in dry ether (40 c.c.) a solution of methylmagnesium iodide (from magnesium 0.9 g., methyl iodide 4.8 g. and ether, 25 c.c.) was added during 30 minutes with stirring and cooling in an ice-bath. The reaction mixture was allowed to attain room temperature during 2 hours with occasional swirling; finally it was refluxed for 3 hours and left overnight at room temperature. The reaction mixture was well-chilled in an ice-salt bath and decomposed by the addition (15 minutes) of dilute HCl (1:1, 30 c.c.). The reddish ether layer was separated and the aqueous phase extracted with benzene (10 c.c. × 3). The combined extracts were washed with brine and dried (Na_2SO_4). On removal of the solvent, a pale, orange viscous residue (5 g.) was left, which was distilled to afford a viscous liquid, b.p. 153-55°/1 mm., yield 2.5 g. The material was insoluble in sodium bicarbonate solution, but soluble in hot aqueous sodium hydroxide solution.

A mixture of the above lactone (2.1 g.), hydriodic acid (7 c.c., *d* 1.7) and red phosphorus (1.4 g.) was gently refluxed in an oil-bath at 130°-140° for 24 hours. The reaction mixture was diluted with water (50 c.c.) and extracted with benzene-ether mixture (1:1; 20 c.c. × 3). The extracts were washed with water (10 c.c.), saturated sodium bicarbonate solution (10 c.c. × 2) and finally with brine (10 c.c. × 2). The acidic material (0.5 g., b.p. 157°/1 mm., presumably VII), isolated in the usual manner, was not studied further. From the sodium bicarbonate-washed solvent extracts, the neutral *tetralone* was isolated as a colorless mobile liquid, b.p. 128°-31°/1.5 mm., n_D^{25} 1.5395, yield 1.0 g. (50%).

1:4:5-*Trimethyl*-7-*isopropyl*-5:6-*dihydronaphthalene* (X).—The tetralone [VIII: method *i*; 7.5 g.], dissolved in ether, was let into (5 minutes) a stirred (Mag-mix) and cooled (0°) suspension of lithium aluminium hydride (1 g.) in ether (50 c.c.). The reaction mixture was stirred for another 30 minutes, while the contents were allowed to attain room temperature (25°) during this period. This was decomposed with ice water (50 c.c.), followed by ice-cold dilute sulphuric acid (10%; 100 c.c., 30 minutes) in the usual manner. The solvent layer was separated and the aqueous phase extracted with ether (20 c.c. × 3). The combined extracts were washed with sodium bicarbonate solution and then with brine and dried (Na_2SO_4). Removal of the residue gave a distillate with a wide boiling point range (113°-143°/2 mm., yield 6.6 g.) due to partial dehydration of the tetralol during rectification. This was completely dehydrated as shown below.

The above material (6.6 g.) and iodine (30 mg.) were heated together on a steam-bath for one hour, when water separated out readily. To this benzene (10 c.c.) was added, which was fractionated off; this operation was repeated twice to remove azeotropically all the water of dehydration. The residue was taken up in petroleum ether (10 c.c.) and dried over activated silica gel. The solvent was flashed off and the dihydronaphthalene fractionated over sodium as a colorless mobile liquid, b.p. 118-20°/2 mm., yield 5.0 g. (72%). An analytical cut had n_D^{24}, 1.5485; d^{24}_4, 0.9393; M_D, 72.4 (calc. M_D, 69.84; EM_D, 2.56; $E\Sigma_D$, 1.2) (Found: C, 88.84; H, 10.2. $C_{16}H_{22}$ requires C, 89.72; H, 10.28 per cent).

4:5-*Dimethyleudalene* (XI): (*i*) *From the above Dihydronaphthalene* (X).—The above hydrocarbon (4.8 g.) was dehydrogenated with sulphur (0.74 g.) by the method

described above for 4:8-dimethyleudalene (VI), and the crude product was similarly purified *via* its recrystallised (ethanol) *TNB complex*, as golden yellow needles, m.p. 144°, yield 3.3 g. (Found: N, 9.71. $C_{22}H_{23}O_6N_3$ requires N, 9.86 per cent). The pure 4:5-*dimethyleudalene* (XI), as obtained by regeneration from the above complex, had b.p. 138-39°/2.5 mm., $n_D^{28.5}$ 1.5840, $d_4^{24.5}$, 0.9706, M_D 73.1 (calc. M_D 69.37, EM_D 3.73, $E\Sigma_D$, 1.76); yield 1.55 g. (Found: C, 90.79; H, 9.50. $C_{16}H_{20}$ requires C, 90.57; H, 9.43 per cent).

The *picrate* after two crystallisations from ethanol came out as orange-red needles, m.p. 119.5°. (Found: N, 9.6. $C_{22}H_{23}O_7N_3$ requires N, 9.52 per cent).

The *TNF complex* was crystallised four times from 80% acetic acid, when it separated as beautiful red needles, m.p. 143°. (Found: N, 7.96. $C_{29}H_{25}O_7N_3$ requires N, 7.98 per cent).

The *TNA additive compound* was thrice crystallised from ethanol to furnish deep yellow needles, m.p. 161°. (Found: N, 12.34. $C_{22}H_{24}O_6N_4$ requires N, 12.73 per cent).

The *trinitrotoluene complex* on two crystallisations from ethyl alcohol yielded yellow needles, m.p. 53°. (Found: N, 9.56. $C_{23}H_{25}O_6N_3$ requires N, 9.57 per cent).

(*ii*) *From the Tetralone* (VIII) *prepared from* (I).—The identification of the tetralone prepared from (I) with that of the ketone obtained from (VII) was carried out by its conversion into the 4:5-dimethyleudalene (XI).

The neutral ketonic material (0.75 g.) in alcohol (12 c.c.) was reduced with sodium (1.0 g.) in the usual manner. The crude material (0.55 g.) was directly dehydrogenated with sulphur (70 mg.) as described above. The product was taken up in petroleum ether (2 c.c.) and filtered through a column of alumina (Basic/I; 18 g.). This was washed with petroleum ether (30 c.c.). The solvent was flashed off and the residue converted into the *TNB complex*, which was twice crystallised from ethanol as yellow needles, m.p. 144°; mixed m.p. with the earlier sample obtained by the other route was undepressed.

The authors are thankful to Dr. M. S. Muthana for showing interest in these investigations.

ORGANIC CHEMISTRY DEPARTMENT,
INDIAN INSTITUTE OF SCIENCE,
BANGALORE.

Received December 15, 1955.

[Jour. Indian Chem. Soc., Vol 33, No. 8, 1956]

THERMAL DECARBOXYLATION OF CHLOROBENZOIC ACIDS

By S. S. Muhammed and Miss Aziz Siddiqui

Thermal decarboxylation of *o*-chloro- and 2-4-dichlorobenzoic acids in resorcinol solution follows S_E2 mechanism. The activation energies, frequency factors and entropies of activation are: 32300 cals. mole $^{-1}$, 6.76×10^{10} sec. $^{-1}$ and -12.0 cals. deg.$^{-1}$ for *o*-chlorobenzoic acid, and 27600 cals mole^{-1}, 3.98×10^{9}sec.$^{-1}$ and -17.6 cals. deg.$^{-1}$ for 2:4-dichlorobenzoic acid.

In continuation of our work on benzoic acid (this *Journal*, 1954, **31**, 726) we present the results of our studies on *o*-chloro- and 2:4-dichlorobenzoic acids.

Experimental

The apparatus was the same as reported earlier and the procedure was also similar excepting that instead of reading the total volume of CO_2 evolved at the completion of reaction, Guggenheim's method (*Phil. Mag*, 1926, **2**, 538) was employed to obtain the first order rate constants. Two series of values, V and V', for the volumes of carbon dioxide at times t and t', separated by a constant interval Δt, were obtained at different times 't'. A plot of $\log_{10}(V'-V)$ against 't' gave a straight line, the slope of which was equal to 0.4343 × rate constant. Typical data on decarboxylation of *o*-chlorobenzoic acid in resorcinol at 237° are shown in Table I.

Table I

Time (t).	V of CO_2 at t.	V' of CO_2 at $(t+\Delta t)$.	Diff. $(V'-V)$	Log $(V'-V)$.
0 min.	0.6 c.c.	19.4 c.c.	18.8 c c.	1.2742
2	12.3	26.8	15.5	1.1903
4	19 4	32.4	13.0	1.1139
6	26.3	37.6	11.3	1.0531
8	31.4	40.6	9.2	0.9638
10	38.6	46.2	7.6	0.8808
12	41.6	48.1	6.5	0.8129
14	45.2	50 6	5.4	0.7324

The plot of log $(V'-V)$ against t gave a straight line, the solpe of which, when multiplied by 2.303 and divided by 60, provided the rate constant as 143.95×10^{-5} sec.$^{-1}$ at 237°. Further determinations at this temperature furnished the values: 134.21, 115.83, 126.48, 123.74($\times10^{-5}$). The mean of these five (128.84×10^{-5} sec.) was taken to be the rate constant at 237°. Similar data were collected for *o*-chlorobenzoic acid at three other temperatures (249°, 224° and 218°). The same procedure was repeated for 2:4-dichlorobenzoic acid at 192°, 201°, 211° and 220°. Table II records the values of rate constants for the two acids at different temperatures.

TABLE II

o-Chlorobenzoic acid.		2 :4-Dichlorobenzoic acid.	
Temp.	Rate const. $k \times 10^5$ per sec	Temp.	Rate const. $k \times 10^5$ per sec.
218°	37.58	192°	52.72
224°	55.66	201°	91.41
237°	128.84	211°	166.08
249°	255.02	220°	280.50

The plot of log k vs. $1/T$ was used in deriving the activation energies of the two acids. The frequency factors, A, were computed with the help of the Arrhenius equation :

$$k = A.e^{-E/RT}$$

substituting the experimental values of the rate constants k and activation energies, E. The thermodynamic characteristics of activation were calculated from the following relations (using the notations of Glasstone, Laidler and Erying, "The Theory of Rate Processes") :

$$\Delta F \neq = 2.303\, RT \log (RT/Nhk)$$
$$\Delta S \neq = (\Delta E \neq - \Delta F \neq)/T$$

In these calculations the heat of activation $\Delta E \neq$ was taken to be equal to $(E - RT)$ where E is the experimental activation energy.

The activation energies, frequency factors, free energies and entropies of activation are shown in Table III.

TABLE III

		o-Chlorobenzoic acid.	2 :4-Dichlorobenzoic acid.
Activation energy (E)	...	32360 cals. mole^{-1}	27600 cals. mole^{-1}
Frequency factor (A)	...	6.76×10^{10} sec^{-1}	3.98×10^{9} sec^{-1}
Free energy of activation (at 493°K) ($\Delta F \neq$)	...	37200 cals. mole^{-1}	35300 cals. mole^{-1}
Entropy of activation (at 493°K) ($\Delta S \neq$)	...	-12.0 cals. deg.$^{-1}$	-17.6 cals. deg.$^{-1}$

DISCUSSION

The results presented above clearly show that like benzoic acid (*loc. cit.*), *o*-chloro- and 2:4-dichlorobenzoic acids are unstable in acidic solution, indicating that these acids undergo thermal decarboxylation through a bimolecular mechanism, involving the electrophilic replacement of $(COOH)^+$ from the acid :

$$H^+ + -C - C\langle^{O}_{OH} \rightarrow -CH + \left(C\langle^{O}_{OH}\right)^+$$

A comparison of the three acids reveals that whilst benzoic acid decarboxylates at 255° with a velocity of only 30.3×10^{-5} sec.$^{-1}$, the extrapolated values at this temperature for *o*-chloro- and 2 :4-dichlorobenzoic acids are 375×10^{-5} and 966×10^{-5} respectively. Further, the activation energies for these acids progressively decrease from 42500 (benzoic acid) and 32300 (*o*-chlorobenzoic acid) to 27600 cals. (2 :4-dichlorobenzoic acid). This

may be explained on the assumption that S_E2 mechanism is facilitated by a high electron density on the α-carbon. The presence of chlorine in the *ortho* (or *para*) position increases the negative character of the α-carbon, which therefore attracts the proton or protonated solvent more readily, and undergoes decarboxylation rapidly. Further, the presence of two chlorine atoms in *ortho* and *para* positions in the 2:4-dichlorobenzoic acid enhances the negativity of the α-cabon, and hence, the latter acid decomposes much faster than the *ortho*-acid. This explanation is directly in line with the views of Brown, Hammick and Scholefield (*J. Chem. Soc.*, 1950, 778). The other explanation which is helpful here is that of Schubert (*J. Amer. Chem. Soc.*, 1949, **71**, 2639) who suggests that due to the presence of substituents, the resonance interaction of the carboxyl with the ring is inhibited, which leads to the weakening and consequent breaking of the bond between carboxyl and the α-carbon.

Now we may also compare the frequency factors and activation entropies of benzoic acid (8.7×10^{12} sec^{-1} and +2.1 cals.$deg.^{-1}$ at 255°), calculated from the data of our previous paper (*loc. cit.*) with *o*-chloro- and 2:4-dichlorobenzoic acids, shown in Table III. The continuous decrease in these values indicates a continuous fall in the steric factor which determines the probability of reaction. This is similar to the observation of Brown *et al.* (*loc. cit.*) and may be explained on the assumption of a steric effect. The chlorine atom in the *ortho* position, while enhancing the negativity of the α-carbon, may itself try to attract the proton, which means that the attack on the α-carbon will not be so facile as pictured earlier. Further, in 2:4-dichlorobenzoic acid the two chlorine atoms present are likely to inhibit to a greater extent the approach of the proton to the α-carbon, thus accounting for still lower frequency factor and lower entropy of activation.

One of the authors (A.S.) has to acknowledge her gratitude to the Government of India for the award of a research fellowship, which enabled her to carry out the experimental part of this paper.

CHEMICAL LABORATORIES,
OSMANIA UNIVERSITY,
HYDERABAD-DECCAN.

Received January, 16, 1956.

[Jour. Indian Chem. Soc., Vol. 33, No. 8, 1956]

PAPER IONOPHORESIS OF SOME PURINES AND PYRIMIDINES *

By S. N. Mukherjee and (late) A. R. Ghosh

The paper ionophoresis of the common purines and pyrimidines of nucleic acids has been carried out in presence of an acid, an alkali and a phosphate buffer of p_H 2.2, both in the horizontal and vertical set-ups, as proposed by McDonald and Durrum. It has been shown that reproducible results can be obtained if the experiment is carried out under strictly controlled conditions so that there is no evaporation of liquids. Loss of water by evaporation from the surface of the paper brings in complications like endosmos s, chromatographic flow, etc. This evaporation can be stopped by keeping the current small and applying feed to the filter paper at regular intervals.

In a previous communication (Ghosh and Burma, *Science & Culture*, 1953, **19**, 103) the ionophoretic behaviour of the major purine and pyrimidine constituents of nucleic acids (viz., adenine, guanine, cytosine, thymine and uracil) in the vertical migration method of Durrum (*J. Colloid Sci.*, 1951, **6**, 274) in a phosphate-citric acid buffer of p_H 2.2 and $N/10$-NaOH solution has been reported, but the results are different in the experiments performed according to the horizontal migration technique of McDonald (*J. Chem. Ed.*, 1952, **29**, 428). Such lack of agreement has also been reported by Durrum and McDonald in the vertical and horizontal ionophoresis experiments with amino-acids. Durrum (*J. Amer. Chem. Soc.*, 1951, **73**, 4875) has not been able to achieve linearity of movement of migrants with time, which has been observed by McDonald (*loc. cit.*). Further, Durrum (*Fed. Proc.*, 1950, **9**, 166) has observed the phenomenon of "mobility equilibrium" with certain amino-acids, but McDonald has not. In view of these discrepancies, a detailed study of the paper ionophoresis of the above substances in the two migration techniques has been undertaken in solution of ionic strength of the order of 0.1.

Experimental

The horizontal ionophoresis apparatus was assembled according to the directions of McDonald (*loc. cit.*) but with two modifications: (*i*) the ends of the paper strips were dipped in separate vessels which were connected to the two electrode vessels by agar —KCl bridge, the purpose being to protect the migrants from the unfavourable p_H changes owing to accumulation of the electrode products; (*ii*) an arrangement for feeding at the apex (28 cm. high in our apparatus) was incorporated with the help of separate paper strips hanging over the glass support and dipping in separate vessels which contained the same electrolyte solution and were connected to the electrode vessels by the salt bridge.

The purine and pyrimidine compounds, of the purest quality available, were freshly dissolved in the same solutions as used in ionophoresis experiments (concentration being about 5 mg./c.c. in all cases). Ionophoresis was normally allowed to continue

* A note on this topic was published by late A. R. Ghosh in *Naturwiss.*, 1954, **11**, 257.

for 8 hours at 220 volts at 25° ± 0.5°. For each experiment about 0.02 c.c. of the migrant solution was applied on paper strips (1 cm. in width) which had been previously soaked in the electrolyte solution and kept in position within the apparatus for an hour with the current passing for equilibration. The possibility of movement of liquid due to some irregularity in the experimental arrangements is ruled out by the complete absence of movement of the migrants without current passing. For detection of the purines and pyrimidines on the paper, the well-known fluorescence quenching technique of Holiday and Johnson with the help of the 'chromatolite' lamp was employed.

Three solutions were selected as conducting media: (*i*) phosphate-citric acid buffer (McIlvaine's buffer) of p_H 2.2 for separation of adenine, guanine and cytosine (cf. Ghosh and Burma, *loc. cit.*); (*ii*) $N/10$-NaOH solution for separation of thymine and uracil (*ibid.*); and (*iii*) $N/10$-H_2SO_4 solution for purposes of comparison with the alkali solution.

Experiments in Caustic Soda Solution.—In $N/10$-NoOH solution as the electrolyte, it was found that in the horizontal procedure adenine, guanine, thymine and uracil moved towards the positive electrode from different initial points of application, although the movement was neither linear with time, nor constant along the length of the paper; the approximate distances moved from the centre were: adenine 4-5 cm., guanine 4.5-5.5 cm., thymine 9-10 cm. and uracil 11-12 cm. Cytosine, however, moved towards the centre from the two ends, while from the centre it moved slightly towards the anode; further, the extent of movement was greater as the ends were approached. Current passing per strip was about 1 mA at the start, but increased to about 2 mA at the end of 8 hours. Water was found to collect on the inner walls of the enclosing vessel, evidently as a result of distillation from the solution. In the vertical arrangement, cytosine did not move from the apex while the other bases moved towards the anode from that position; the approximate distances were: adenine 4-5 cm., guanine 6-7 cm., thymine 6-7 cm. and uracil 8-9 cm. From other initial points of application, all the five migrants (cytosine most pronouncedly) moved towards the apex. Current passing was initially almost the same as in the horizontal arrangement, but the final value was slightly greater. The peculiar behaviour of cytosine will be evident from the following data, which are the averages of three well-agreeing experiments.

TABLE I

*Movement of cytosine in $N/10$-NaOH soiution.**

Initial position of the migrant.	Direction and extent of migration. Horizontal.			Vertical.		
26 cm. from centre towards (+ve) electrode	8.8 cm.	towards	−ve elec.	10.1 cm.	towards	−ve elec.
13 „ „ „ „ „ „	3.7	...	−ve	5.2	...	−ve
At the centre	0.7	...	+ve	0.2	...	+ve
13 cm. from centre towards (−ve) electrode	5.3	...	+ve	6.0	...	+ve
26 „ „ „ „ „ „	10.6	...	+ve	11.2	...	+ve

*Potential gradient was 6.1 volt/cm.

*Experiments in Sulphuric Acid Solution.**—The tendency of the spots, applied away from centre, to move towards that region was again evident in experiments with $N/10$-H_2SO_4 solution, more so in the vertical than in the horizontal method; the spots applied at the centre, however, moved towards the cathode. Current passing increased approximately from 0.8 to 1.7 mA per strip during 8 hours and considerable distillation of water was noticed. The observed movements from the centre were approximately (*vertical*): adenine 6-7 cm., guanine 5-6 cm., cytosine 6-7 cm., thymine 6-7 cm., and uracil 5-6 cm.; (*horizontal*): adenine 5-6 cm. guanine 5-6 cm., cytosine 6-7 cm., thymine 4·5 cm., and uracil 4·5 cm.

*Experiments in the Buffer Solution**.—In the buffer solution of p_H 2.2, the movement of adenine, guanine and cytosine was towards the cathode, linear with time, constant along the length of the paper and identical both in the horizontal and vertical arrangements; thymine and uracil did not practically show any movement. Current passing per strip was throughout 0.15 mA in both the set-ups. Even when the electrodes were directly dipped into the same vessel as contained the ends of the paper strips, the change in p_H in 8 hours was only 0.01-0.04 units; the distillation of water was not perceptible even when the feeding arrangements were eliminated. Table II records the migration data (the average of three experiments) of the substances in this buffer.

TABLE II

*Movement in buffer solutions of p_H 2.2 in 8 hours' time***.

Initial position of the migrant.	Direction and extent of migration to the cathode									
	Horizl.	Vertl.	Horizl.	Vertl.	Horizl.	Vertl.	Horizl.	Vertl.	Horizl.	Vertl.
	(*a*) Adenine.		(*b*) Guanine.		(*c*) Cytosine.		(*d*) Thymine.		(*e*) Uracil.	
20 cm. from centre towards the anode	6.4 cm.	6.4 cm.	6.0 cm.	6.2 cm.	7.0 cm.	6.8 cm.	0.10 cm.	0.08 cm.	0.0 cm.	0.0 cm.
At the centre	6.5	6.0	6.2	6.0	7.0	7.1	0.0	0.1	0.1	0.0
20 cm. from centre towards the cathode	6.9	6.1	6.3	6.2	6.9	6.9	0.15	0.0	0.05	0.1

**Ionic strength = 0.1 and potential gradient = 1.1 volt/cm.

Mobility Experiments.—When ionophoresis was allowed to continue for longer time, mobility equilibrium phenomenon was observed in some cases. In caustic soda solution all the migrants in the vertical, but only cytosine in the horizontal arrangement came to equilibrium from different initial points of application after about 24 hours at positions slightly away from the apex towards the anode. In the sulphuric acid solution the phenomenon was observed with all the migrants in both the techniques, the equilibrium positions being slightly away from the centre but now towards the cathode. It should be pointed out that with these two solutions as media, considerable distillation of water took place during the experiments and simultaneously the current passing increased considerably. In the buffer solution studied, no such equilibrium was noticed.

*Ionic strength = 0.1.

TABLE III

Mean migration in 8 hours' time in a buffer solution of p_H 2.2.
Ionic strength of 0.1 and potential gradient = 1.1 volt/cm.

Substances.	Movement towards.	Horizontal.	Vertical.
Adenine	Cathode	6.60 cm.	6.20 cm.
Guanine	,,	6.20	6.10
Cytosine	,,	6.05	6.00
Thymine	,,	0.08	0.06
Uracil	,,	0.05	0.03

DISCUSSION

In order to investigate the reasons for the discrepancy in the two sets of results, the interfering effects of adsorption and electro-endosmosis, if any, on the electrophoretic migration may be neglected since they would be the same in both the techniques. It was, however, noticed that due to passage of current (of the order of 1 mA or more per strip) appreciable heat was developed resulting in gross distillation of water from the vessels as well as from surface of the paper; this increased the electrolyte concentration in the experimental solution, affecting thereby its electrical resistance and ionic strength. Further, as a result of heating the portion of the filter paper, away from the supply vessels, became dry, thus causing the capillary forces to continually siphon fresh solution to those regions. Durrum (*loc. cit.*) has pointed out that this phenomenon results in a flow-rate gradient which decreases towards the centre of the paper. He has explained the mobility equilibrium, exhibited by certain ions in the vertical experiments, to be due to the equilibrium between the velocity of true electrophoretic migration and that of the counter-current flow of electrolyte towards the centre of the paper. The latter velocity depends upon the experimental arrangements and is superimposed on the true ionophoretic mobility of the migrants ; further, this velocity varies in magnitude and direction along the length of the paper and also changes during the course of the experiments.

In McDonald's procedure, because of the arrangements of elaborate feeding and efficient dissipation of heat, the drying phenomenon is not perceptible ; so the effect of the above-mentioned secondary liquid flow is negligible and the movements are thus normal as exhibited by the linearity with time and the absence of "mobility equilibrium" phenomenon. But in Durrum's (*loc. cit.*) original experiments no such arrangements are made ; so the drying of the paper, giving rise to secondary liquid flow, brings about the abnormalities. That the equilibrium positions of Durrum's migrants are not their true characteristics, but are dependent principally upon the experimental arrangements, is shown by the observation of Durrum himself (*loc. cit.*) that the equilibrium positions are shifted as a result of a profound change in electrolyte concentration after very prolonged electrophoresis.

In our experiments with alkali solution, the tendency of the migrants to move in a direction opposite to that expected from electrophoresis is always attended with heat-

ing and appreciable distillation of water, and evidently the result of secondary liquid flow. The greater movement (towards the centre) of substances applied near the cathode than that when applied at corresponding positions near the anode, as experimentally observed, is probably due to the fact that in the former case the velocities augment, while in the latter they oppose each other. Owing to better feeding arrangements the abnormality is much less in the horizontal technique than in the vertical one ; this explains the slight movement of cytosine from the centre in the horizontal arrangement compared to almost none from the apex in the vertical ; but the slight deviation of the movements from linearity with time and from constancy at different regions of the paper in the horizontal arrangement testifies that the irregularities, though much reduced, still exist. The exceptional behaviour of cytosine in alkali solution in moveing towards the centre from both sides, even in the horizontal experiment, is probably due to a very small electrophoretic mobility of this migrant in the medium used. The results in the sulphuric acid solution can be explained in an analogous manner. In the buffer solution, because of the low constant current, the disturbing factors are completely absent, and the movements are perfectly normal and in conformity with theoretical expectations. The phenomenon of mobility equilibrium in our experiments can also be explained in this light. The experimental observation that the two equilibrium positions of a particular migrant in a particular solution in the two techniques do not exactly coincide with each other is theoretically expected because of different values of the secondary liquid flow in the two arrangements.

Further Experiments in support of these views.—The above mentioned irregularities may be expected to be eliminated in the apparatus of Kunkel and Tiselius (*J. Gen. Physiol.*, 1951, **35**, 89) with the paper strips enclosed without gap between two glass plates clamped air-tight, thus preventing evaporation of liquid or in that of Markham and Smith (*Nature*, 1951, **168**, 406), with the paper strips bent in the form of the letter V and immersed in water-immiscible, non-polar liquid to dissipate the heat generated by electrophoresis. Experiments employing these techniques or a slightly improved one with the paper strips held horizontally within a tube filled with the non-polar liquid, it was found that the migrants even from extreme initial positions never moved in a direction opposite to that expected ; the mobility values, however, could not be accurately determined due to the spots being diffuse.

In experiments with quinine as migrant (the movement being detected by its fluorescence under the 'chromatolite' lamp) it was found that in decinormal sulphuric acid solution, it came to equilibrium in the vertical experiments, but in the horizontal arrangement it moved always towards the cathode, though neither linearly with time nor regularly along the length of the paper. In view of the greater irregularity in the vertical arrangement, these observations are easily explainable. With quinine, alkaline media were avoided due to multiplicity of the spots. With buffer solution of p_H 2.2, the migrant, as expected, was found to move towards the cathode quite regularly and to the same extent both vertically and horizontally.

Later on, by keeping the current sufficiently low and constant within 0.1 mA per strip with the help of adjustable resistance in the circuit and maintaining a more uni-

form water sheath on the paper, even in the vertical arrangement, by more frequent feeders, distillation of water was found to be much less in 8 hours in both alkaline and acidic media ; the movement of migrants in a direction opposite to that expected from electrophoretic conditions never occurred, thus ruling out the possibility of the phenomenon of mobility equilibrium. The mobility values were also less irregular than the previous ones, though not perfectly normal.

Thus, the controversy between McDonald and Durrum regarding the constancy of mobility with time and the related phenomena in the two techniques of paper ionophoresis studies appears to be principally due to different types of experimental set-ups used by them and consequent differences in the conditions of operation.

PHYSICAL CHEMISTRY LABORATORIES,
JADAVPUR UNIVERSITY,
CALCUTTA-32.

Received March 1, 1956.

[Jour. Indian Chem. Soc., Vol. 33, No. 8, 1956]

CONSTITUENTS OF *CENTALLA ASIATICA*. PART I. EXAMINATION OF THE CEYLONESE VARIETY

By S. C. Bhattacharyya

Centalla asiatica from Ceylon has been found to contain salts, sugar, essential oils and a nitrogen- and sulphur-containing pectin. The most characteristic components are, however, three polyhydroxy triterpenic acids, viz., centic, centoic and centellic acids, and a water-soluble glycoside, centelloside, the aglycone of which is identical with centellic acid.

The plant *Centaila asiatica*, Linn., also known as *Hydrocotyle asiatica*, occupies an important place in the indigenous system of medicine. The botanical details of the plant have been recorded by Hooker ("Flora of British India", 1879, Vol. II, p. 669) and Trieman ("Flora of Ceylon", 1894, p. 226).

Centalla asiatica has been preliminarily examined by Indian workers (Basu and Lamsal, *Quart. J. Pharm. Pharmacol.*, 1947, **20**, 135). From the Madagaskar variety of the same plant, French workers isolated a crystalline, sugar ester-type triterpenoid glycoside ($C_{54}H_{88}O_{22}$, M.W. 1105.2), having a remarkable curative effect against leprosy (*Nature*, 1945, **155**, 601; *Lancet*, 1945, 337; *Brit. Med J.*, 1945, 338; Bontems, *Bull. Sci. Pharmacol.*, 1941, **49**, 186; cf. Lederer *et al.*, *Nature*, 1949, **163**, 258). On hydrolysis it produced two molecules of glucose, two molecules of rhamnose and a molecule of a triterpenic aglycone, asiatic acid ($C_{30}H_{48}O_5$), containing a tertiary carboxyl group and three hydroxyl groups, two of which were in the form of an α-glycol linkage. The sugar residue in the molecule was attached to the carboxyl group by an unusual ester-linkage and, in contradiction to the tertiary nature of the carboxyl group, was hydrolysed easily by both acid and alkali.

Simultaneously with the French workers, work was started by the author in the University Chemical Laboratory, Cambridge, on the Ceylonese and Indian varieties of the plant. Some of the results of investigation on the Ceylonese variety have appeared in earlier publications (*Nature*, 1949, **163**, 259); details are being recorded in this communication.

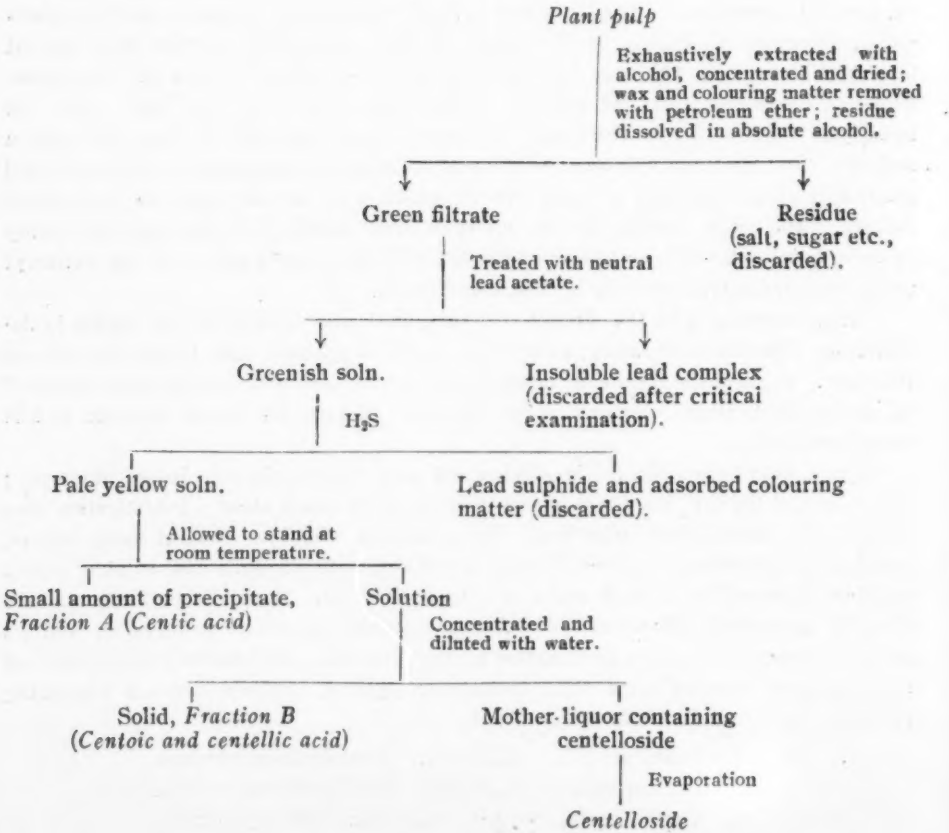
The plants were collected in Ceylon and were dried in the sun before shipment; the weight of the dry plant was about 10-13% of the fresh plant. Investigation was initiated 7-8 months after collection. The plant was found to contain salts, sugars, essential oils and a large amount of pectin containing both nitrogen and sulphur which could be separated into a basic and a non-basic fraction. None of these fractions were critically examined. However, like the triterpenoid glycoside, asiaticoside, and its aglycone, asiatic acid, of the Madagaskar variety, the most characteristic components of the Ceylonese samples were three monobasic, typical, tertiary-carboxyl containing polyhydroxy triterpenic acids, viz.,

1. Centic acid, $C_{30}H_{48}O_5$, three hydroxyl groups.
2. Centoic acid, $C_{30}H_{48}O_6$, four hydroxyl groups.
3. Centellic acid, $C_{30}H_{48}O_6$, four hydroxyl groups.

Most possibly, due to enzymatic hydrolysis, the seven-month old sample of the dried plant did not contain much of glycoside. However, a four-month old and sun-dried sample of the plant and also an alcoholic extract of the fresh plant were found to contain a considerable amount of a water-soluble glycoside, the aglycone of which was identical with centellic acid. This glycoside has been named as "Centelloside." As regards the other constituents, there was no fundamental difference among the various samples.

The three triterpenic acids of the Ceylonese variety were similar but different from asiatic acid, and the glycoside, centelloside, from that of asiaticoside. This has been tested by direct comparison with asiaticoside and asiatic acid. Whereas centelloside was extremely soluble in water, asiaticoside was insoluble in the same solvent. However, there were two very conspicuous points of similarity, viz., (*i*) Like asiaticoside, centelloside was also a sugar ester-type compound and was very easily hydrolysed by both acid and alkali.

SCHEME I

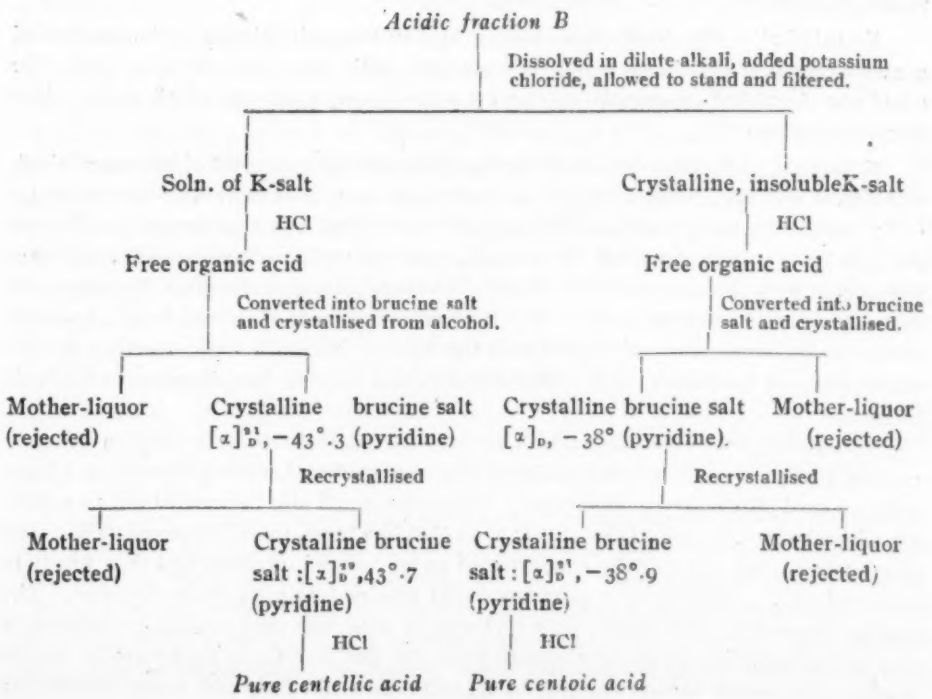

Plant pulp
Exhaustively extracted with alcohol, concentrated and dried; wax and colouring matter removed with petroleum ether; residue dissolved in absolute alcohol.
Green filtrate
Residue (salt, sugar etc., discarded).
Treated with neutral lead acetate.
Greenish soln.
Insoluble lead complex (discarded after critical examination).
H_2S
Pale yellow soln.
Lead sulphide and adsorbed colouring matter (discarded).
Allowed to stand at room temperature.
Small amount of precipitate, Fraction A (Centic acid)
Solution
Concentrated and diluted with water.
Solid, Fraction B (Centoic and centellic acid)
Mother-liquor containing centelloside
Evaporation
Centelloside

(ii) Like asiatic acid, all the three acids from the Ceylonese variety also contained an α-glycol linkage, as quantitatively estimated by specific oxidation test with potassium periodate.

The above two properties appear to be characteristic for *Centalla asiatica*, as the Indian variety has also been found to contain components with similar properties. The sugar chain in centelloside is composed of glucose and fructose ; rhamnose, which is a constituent of asiaticoside, is absent. Quantitative examination of the total reducing sugars gave for centelloside the following composition: Centellic acid:glucose:fructose = 1 : 10 : 2 (mol.), suggesting an approximate molecular weight of 2660. The three triterpene acids and the glycoside, centelloside, were isolated from the alcoholic extract of the plant tissue. The outline is shown in scheme I. The glycoside, centelloside, was obtained in quantity if the plant material was not too old. The other constituents were more or less the same in different samples.

Components of Fractions A and B.—Both these fractions were composed entirely of acidic material as shown by their complete solubility in dilute alkali or alkali carbonate. Centic acid contained in fraction A was purified through its crystalline potassium salt. The free acid was however, amorphous and in this respect was similar to asiatic acid with which it was also isomeric, but not identical. Fraction B was composed of centoic acid and centellic acid. These were separated and purified as shown below :

SCHEME II



The overall yields of pure product from 1 kg. of the dried plant tissue were as follows: (*i*) centic acid, 0.3-0.5 g., (*ii*) centoic acid, 4-5 g., (*iii*) centellic acid, 2-3 g., (*iv*) centelloside from four-month old sample, 4-5 g., (*v*) centelloside from 1 kg. of the fresh plant, 1-2 g. Centoic acid was the major acidic component and it could also be handled comparatively easily, as its derivatives were less soluble compared to those of centellic acids. It should be noted that, possibly due to the presence of too many hydroxyl groups, the three terpenic acids and many of their derivatives, even when analytically pure, were amorphous; their melting points were also not sharp and had to be determined from a preheated bath. In combusting these materials, more time than usual was necessary to obtain concordant results. Equivalent weights could be determined accurately and were checked by parallel titrations with cholic acid. Centoic and centic acids showed correct equivalent weight; centellic acid occasionally gave anomalous results due to retention of solvent, but, doubtlesss, it is also represented by formula $C_{30}H_{48}O_6$.

The glycosides of *centalla asiatica* are somewhat similar in structure to the lipoids of acid-fast bacteria which are not glycerides of fatty acids but esters of fatty acids with carbohydrates (Anderson, Fortschritte der chem. Org. Naturst", Vol. III, 1948, pp. 145, 163).

Experimental

Aqueous extraction.—Cold aqueous extraction of the plant afforded mostly reducing sugars, salts and a small amount of pectin.

Essential oil.—The dried plant pulp (1 kg.) on steam-distillation (7 hours) yielded a steam-condensate (11 litres) which on extraction with ether and working up in the usual way furnished an essential oil (1.0 g.) with a grassy smell and which showed signs of crystallisation.

Extraction of Pectin.—The swollen plant pulp, left after removal of the essential oil, was filtered and the residue extracted by heating for one hour with two lots of water (2 × 5 litres). The combined extract (15 litres) after initial filtration through muslin was clarified by a supercentrifuge. It was concentrated under reduced pressure to 4 litres and diluted with absolute alcohol (8 litres). The precipitated pectin after filtration and drying at 80°-90° weighed 79.0 g. It contained both nitrogen and sulphur. A sample of this pectin (10 g.) was subdivided with the help of HCl to a basic fraction (8.1 g.) and a non-basic fraction (1.0 g.). Both nitrogen and sulphur were present in the basic fraction.

Extraction with hot alcohol: Isolation of Triterpenic Acids & the Glycoside.—The powdered plant tissue (1 kg.) was exhaustively extracted with alcohol (8 litres) in a large stainless steel Soxhlet-type apparatus. Extraction could also be carried out by refluxing with adequate quantity (3 × 5 litres) of alcohol in a large round-bottomed flask. The deep green extract was initially concentrated under reduced pressure and then finally in an open basin. On cooling, a pasty semisolid residue (100 120 g.) was obtained. The residue, as such or after mixing with acid-washed sand, was then extracted continuously in a Soxhlet apparatus with petroleum (b.p. 40°-60°/60°-80°) for at least 6 hours. A very considerable portion of the colouring matter and most of the fatty and waxy constituents

were removed by this procedure. The residue in the thimble after drying at 60° was a hard, brittle mass (50-60 g.). After powdering, it was refluxed with absolute alcohol (2 litres) and the insoluble residue of salt and sugar (14 g.) removed by filtration. The filtrate was diluted with water to bring the strength of alcohol to about 90%. The alcoholic solution was boiled on the water-bath and to it a hot boiling solution of neutral lead acetate (40 g. in 80% alcohol, 500 c.c.) was gradually added. A thick, heavy, deep green precipitate was formed. The reaction mixture after boiling for 30 minutes was filtered hot and the precipitate on the filter bed washed with boiling 80% alcohol (500 c.c.). The green lead complex after critical examination was discarded as no useful product could be isolated from it.

From the alcoholic filtrate (3 litres), which was now only pale green in colour, excess of lead was removed as lead sulphide. The reaction mixture was refluxed for 20 minutes, filtered hot and the precipitate of lead sulphide washed with hot alcohol (200 c.c.). The combined mother-liquor was now only pale yellow in colour [if the removal of colouring matter is not complete, a second precipitation with a small amount (about 10 g.) of lead acetate may become necessary]. It was concentrated to about 2 litres and left at room temperature overnight when a slight precipitate was formed. After separation of this precipitate (0.5 g.—1.0 g. *Fraction A, centic acid*), the mother-liquor was concentrated to 50 c.c. and diluted with water (500 c.c.) when copious amount of light yellow precipitate was deposited. On cooling in the refrigerator overnight, the solid material (10-12 g. *Fraction B, centoic acid* and *centellic acid*) was collected by filtration. If the plant material was not too old, the mother-liquor on complete evaporation afforded the glycoside, centelloside (4-5 g.).

Treatment of Fraction A : Isolation of pure Centic Acid.—Fraction A (4 g. from 5 kg. of the plant) was dissolved in hot water (150 c.c.) containing minimum amount of caustic potash. The solution was heated to boiling and to it solid potassium chloride (15 g.) was added with stirring, when the potassium salt of centic acid crystallised out almost immediately in the form of fine needles. After leaving at room temperature overnight, the salt was collected by filtration and washed with a small amount of saturated KCl solution. Free acid was obtained by decomposition of the salt with mineral acid and further purified by precipitating it from alcoholic solution with water. The yield after drying to a constant weight at 100°/1 mm. was 1.5 g. from 5 kg. of the dried plant tissue. All measurements were made on a sample dried to a constant weight. On a preheated (220°) electrical block, centic acid softened at 230° and became semi-molten at 240° to decompose at 250°-255°. $[\alpha]_D^{28}$, +38°.1 (EtOH ; c = 1.116). It showed positive tetranitromethane test and usual colour reactions with sulphuric acid-nitric acid ; no specific absorption in the U.V. region was found.

Equivalent weight : The following procedure was used to obtain concordant results. Centic acid (50 mg.) was dissolved in hot alcohol (20 c.c.) contained in a 100 c.c. conical flask. Boiling water (14 c.c.) was added, followed by three drops of phenophthalein. The solution was heated to boiling and then quickly titrated to a permanent pink colour with $N/40$-NaOH solution using a microburette calibrated to 1/100 c.c. An identical blank was run side by side. Equivalent weight was checked by determining the same

for cholic acid simultaneously. (Found : Equiv., 490.1 ; C, 73.60 ; H, 10.61. $C_{30}H_{48}O_5$ requires equiv., 488.68 ; C, 73.73 ; H, 9.90 per cent). Equiv. of cholic acid ($C_{24}H_{40}O_5$) found was 410.1 (calc. 408.56). For want of sufficient material this compound could not be examined in details. Its methyl ester, prepared by treatment of a small amount of the material in ether with diazomethane, was resistant to hydrolysis, revealing the tertiary nature of the carboxyl group.

Glycol Linkage in Centic Acid.—Dried centic acid (60.1 mg.) was dissolved by heating in dilute caustic soda (alkali 10 c. c. of $N/40$ in water, 20 c.c.) contained in a measuring flask. $N/40$-H_2SO_4 (11 c.c.) was then added when centic acid was precipitated in the form of a gelatinous mass. Sodium periodate solution (5 c.c., 0.26*M*) was added to the mixture and the content after shaking was left at room temperature. After 24 to 48 hours, the volume was made up to 50 c.c. and titrated in the conventional way with $N/10$ sodium arsenite solution in presence of borax-boric acid buffer ; periodate consumed after 24 hours was 0.91 *M* ; after 48 hours, 0.94 *M* (calc. for 1 α-glycol linkage, 1.0 *M*).

Treatment of Fraction B : Isolation of Centoic Acid and Centellic Acid.—Fraction B(15 g.) was dissolved in 3.5% KOH solution (300 c.c.). The filtered solution was heated to boiling and to it solid KCl (12-15 g.) was added with stirring, and the mixture set aside at room temperature for 24 hours. The potassium salt of centoic acid, which sometimes crystallised out immediately after addition of KCl, was filtered and washed with a little saturated KCl solution. The mother-liquor was kept aside for the isolation of centellic acid. Centoic acid was isolated by decomposition of potassium salt with mineral acid in aqueous suspension. The precipitate of centoic acid was washed with water and then dried at 110°/2 mm. for 2 hours.

Brucine Salt of Centoic Acid.—The crude centoic acid, as obtained above, was dissolved in alcohol containing requisite quantity of brucine. On cooling in a frigidaire overnight, the brucine salt crystallised out in the form of clusters of large plates. On recrystallisation from alcohol, the optical rotation became constant. After filtration the salt was dried to a constant weight at 110°/2 mm., yield 10-11 g. from 15 g. of fraction B. On a preheated (170°) block the salt softened at 190° and gradually formed a glass ; $[\alpha]_D^{31}$, 38°.91 (pyridine ; $c = 1.452$). (Found : C, 70.63; H, 8.50 ; N, 4.21. $C_{53}H_{74}O_{10}N_2$ requires C, 70.8 ; H, 8.3 ; N, 3.1 per cent).

Isolation of Pure Centoic Acid.—To the brucine salt (5 g.), dissolved in hot alcohol (50 ml.), HCl (conc., 3 c.c.) was added, followed by water (250 c.c.). The precipitate of centoic acid was filtered and washed with water. It was redissolved in a little acidulated alcohol and reprecipitated by addition of water, collected as before and dried to a constant weight at 110°/2-3 mm. for 24 hours ; yield 4-5 g. of the pure acid from 1 kg. of the dried plant or 7-10 kg. of the fresh plant. On a preheated block (235°) centoic acid softened at 245° and melted at 256-61° (decomp.). It gave usual colour reactions with tetranitromethane and sulphuric acid-nitric acid ; $[\alpha]_D^{19}$, +43°.51(EtOH ; $c = 0.91$) ; $[\alpha]_D^{19}$, +40°.71 (pyridine ; $c = 3.31$) ; no U.V. absorption.

Equivalent weight was determined as in the case of centic acid. [Found : Equiv., 504.5, 508.3, 505.0, 507.0, 509.8, 506.5, 508.0, 506.5. $C_{30}H_{48}O_6$ requires equiv., 504.68 ; equiv. for cholic acid found : 407.0, 406.0, 407.4, 406.3 (calc. for $C_{24}H_{40}O_5$: 408.56)]. (Found : C, 71.43, 71.84, 71.43, 71.81 ; H, 9.41 ; 10.22; 9.42; 10.32. $C_{30}H_{48}O_6$ requires C, 71.40 ; H, 9.60 per cent).

Methyl Ester of Centoic Acid.—Centoic acid in ethereal suspension on treatment with diazomethane in ether quickly went into solution as methyl ester. After removal of ether the methyl ester was dissolved in acetic acid, precipitated with water, filtered and dried to a constant weight at 100°/1-2 mm. The ester softened at 140° and gave a viscous melt at 150°-155° ; $[\alpha]_D^{19}$, +35°.4 (c=1.046 ; EtOH). (Found : C, 71.93 ; H, 9.78. $C_{31}H_{50}O_6$ requires C, 71.78 ; H, 9.72 per cent). The tertiary nature of the carboxyl group was revealed by the fact that the ester could not be hydrolysed by treatment with acid or alkali.

The Glycol Linkage in Centoic Acid.—Quantitative estimation with periodate was carried out as in the case of centic acid ; periodate consumed was 1.12*M* (calc. 1.0 *M*).

Isolation of Centellic Acid.—The mother-liquor, left after removal of the potassium salt of centoic acid, was heated to boiling and a further quantity of solid KCl (30 g.) added to it. The small amount of the precipitate of the potassium salt of centoic acid was removed by filtration. The filtrate on acidification furnished crude centellic acid. It was purified by converting in alcoholic solution (charcoal) into its brucine salt, which on cooling in a refrigerator for 24 hours crystallised in the form of clusters of needles. Usually two crystallisations were necessary to obtain an optically pure brucine salt which, however, was much more soluble than the brucine salt of centoic acid. It was dried to a constant weight at 110°/2 mm., yield 2.8 g. from 3 g. of crude centellic acid. On a preheated (140°) block, the salt softened at 160°-165° and formed a glass at about 195° ; $[\alpha]_D^{20}$, −7°.87 (c=3.2 ; EtOH) ; $[\alpha]_D^{19}$, −43°.7 (pyridine ; c=1.44). (Found : C, 69.84 ; H, 8.52 ; N, 3.54. $C_{53}H_{74}O_{10}N_2$ requires C, 70.8 ; H, 8.3 ; N, 3.1 per cent).

Free centellic acid was isolated by decomposition of the brucine salt in the usual way and dried to a constant weight by heating at 110°/2 mm. for 24 hours ; yield 2-3 g. of the pure acid from 1 kg. of the dry plant. In a preheated block (220°) it softened at 230° and melted at 234-36° with decomposition. The rate of heating was an important factor. It gave usual colour reactions with tetranitromethane and nitric acid-sulphuric acid ; no absorption was noticed in the U.V. region ; $[\alpha]_D^{19}$, +35°.7 (EtOH ; c= 0.94) ; $[\alpha]_D^{19}$, +32°.1 (pyridine ; c=3.2) ; periodate consumed was 1.1 (calc. for α-glycol linkage : 1.0 *M*). Centellic acid is a very unusual compound ; it retains water and solvent so tenaciously that it is extremely difficult to get concordant analytical results. Some of the values are recorded here. (Found : C, 70.70, 71.92, 71.75, 70.94 ; H, 10.10 ; 10.31, 10.14, 10.50. $C_{30}H_{48}O_6$ requires C, 71.40 ; H, 9.60 per cent). The anomalies were more conspicuous in the case of equivalent weight which varied considerably with different samples, though all of these were otherwise identical and were obtained through optically pure brucine salts. (Eq. wt. found : 533.4 ; 534.9, 528.0, 534.5, 533.8, 535.7, 533.4, 532.8 ; after six months : 524.0, 524.0 ; a fresh sample : 513.5, 513.7, 517.8 519.0 ; another sample : 521.0, 528.2 526.1 ; calc for $C_{30}H_{48}O_6$: 504.7). [Eq. wt. of cholic acid found : 407.0, 406.0, 407.4 ; 402.8 ; 406.3, 405.9, 406.1, 411.8, 407.1 ; calc. for $C_{24}H_{40}O_5$: 408.56]. However, its methyl ester which had less tenacity for solvent gave better analytical results, proving conclusively that centellic acid has the formula $C_{30}H_{48}O_6$. This is also supported by the crystalline brucine salt, described earlier. The methyl ester was prepared in the usual way from the acid and diazomethane and dried at 100°/1 mm. as a white amorphous powder. It softened at 135° and melted at 148-53° ;

$[\alpha]_D^{18}$, + 29°.1 (EtOH ; c=1.258). (Found : C, 71.74 ; H, 10.31. $C_{31}H_{50}O_6$ requires C, 71.78 ; H, 9.7 per cent). The carboxyl group was tertiary, as the ester could not be hydrolysed with acid or alkali.

Isolation of Centelloside.—The glycoside was contained in the ultimate aqueous mother-liquor, left after removal of centoic and centellic acids, as indicated in scheme I. It was present only when the plant material was not too old. The glycoside-containing mother-liquor was usually deep brown in colour. On heating with mineral acid it deposited a gelatinous precipitate, showing the presence of glycoside in solution. For characterisation of the aglycone, the glycoside-containing mother-liquor (500 c.c. ≡ 2kg. of the dried plant) was mixed with H_2SO_4 (20 g. in 20 c.c. water) and boiled gently for 1 hour. There was considerable frothing during boiling and a gelatinous precipitate was formed. It was identified as centellic acid through its brucine salt ($[\alpha]_D^{17}$, −8° ; (EtOH ; c = 3.2) and through other properties. Taking the amount of attached sugar into consideration, there was about 16 g. of centelloside per kg. of the dried or 1.5 to 2.0 g. per kg. of the fresh plant.

Extraction of the fresh plant.—This extract (equivalent to 1 kg. of the fresh plant) was obtained directly from Ceylon. It had deposited a solid during transit which after separation was identified through its brucine salt as centoic acid (0.28 g.). The filtrate this time was clarified with excess of basic lead acetate according to Bontem (*loc. cit.*), and the lead-complex and the mother-liquor were separated. The mother-liquor was treated with H_2S and worked up in the usual way. It contained centelloside, the aglycone of which was characterised by Tripett and Lythgoe (*Nature* 1949, **163**, 259) as centellic acid and the sugar components as glucose and fructose through paper chromatography. The lead complex was also examined by us critically. After decomposing it in alcoholic suspension with hydrogen sulphide, the alcoholic solution was found to contain a triterpene (0 32 g.) which was purified through its brucine salt and identified as centoic acid.

Asiaticoside.—The sample of this crystalline glycoside (0.5 g.), obtained from the French workers, was critically examined. It was also a sugar ester like centelloside and could be hydrolysed with both dilute acid and alkali. The aglycone, asiatic acid, obtained by hydrolysis with dilute alcoholic sulphuric acid (10 c.c. of 5% H_2SO_4 in 30% EtOH) was like the triterpenic acid of Ceylonese variety and had similar properties. It had the same molecular formula as centic acid and like the latter formed a precipitate with neutral lead acetate which was not so soluble in alcohol. Centic acid, which we isolated from the Ceylonese plant pulp, presumably escaped complete precipitation with lead acetate.

The author takes this opportunity of expressing his deep gratitude to Dr. B. Lythgoe and Prof. A. R. Todd of the University of Cambridge where the work was actually carried out.

NATIONAL CHEMICAL LABORATORY,
POONA-8.

Received November 25, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 8, 1956]

AN ANALYSIS OF THE NEUTRALISATION CURVES OF THE COLLOIDAL ACIDS. PART I

By S. L. Gupta

The neutralisation curves of the colloidal acids have been interpreted as the neutralisation of macromolecular polybasic acid particles, as if present in true solution. A method has been suggested for approaching the polybasic acid (containing a single type of acidic groups) neutralisation curve graphically and quantitatively. The initial slope of such a curve is monobasic, and in fact, the whole curve is monobasic everywhere, only the active acidity and the dissociation constant have different values for different points on the curve. As a titration proceeds, the active acidity gradually increases and the dissociation constant drifts to lower and lower values. Whereas in the neutralisation of a monobasic acid in true solution the −ve logarithm of the dissociation constant (pK value) is a fixed point at half neutralisation, here in the case of the polybasic acid it has been found to lie on a smooth continuous curve, the change being nowhere abrupt. Simultaneous ion- adsorption considerably masks this monobasic behaviour and sometimes produces an apparent impression of the presence of a strong acid and also of a discontinuity in the dissociation constant relationship. In many cases the experimental curve is the resultant of two curves, one due to ion adsorption and the other due to neutralisation as in true solution.

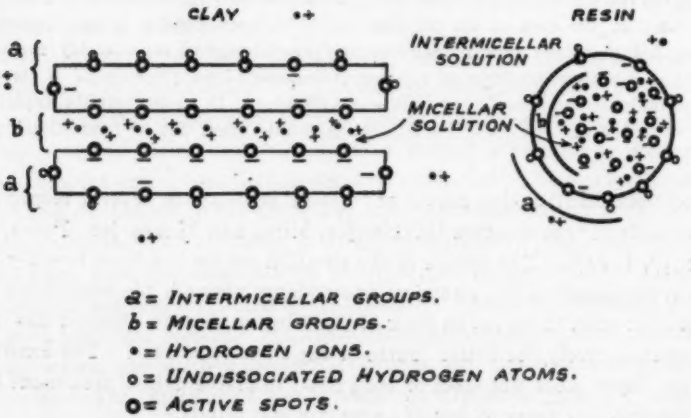
The potentiometric titration curves of colloidal acids are in several respects different from those of acids in true solution (Mukherjee, Mitra and Mukherjee, *Trans. Nat. Inst. Sci. India*, 1937, **1**, 227). The nature of the titration curves has been broadly interpreted on the basis of the theory of the electrical double layer *vis a vis* the interaction of the ions in the double layer with those in the bulk of the solution, but no attempt has been made to interpret quantitatively the entire course of the titration curves. The existing picture of the double layer does not seem to lend itself to mathematical treatment because the parameters involved are more or less of uncertain magnitude.

The present communication records, firstly, a somewhat different picture concerning the interaction between ions in solution and those associated with colloidal particles, and secondly, it derives, based on the above formulation, relationships between the p_H and added alkali concentration, of some of the possible types of the colloidal acids, and finally brings, in the way of verifying the above relationships, some published information on the potentiometric studies of a silicic acid sol.

The proposed picture in a colloidal system, composed of negatively charged particles, envisages a certain degree of aggregation, probably, as a result of the bonding between the exchangeable cations and the colloidal particles. A somewhat similar picture has been invoked to explain the formation of soil crumbs (Russell, *Phil. Trans. Roy. Soc.*, 1934, **233A**, 361), but we have reasons to think that a definite amount of aggregation always exists even in apparently well-dispersed sols, viz., clay sols. No account has been taken, in the proposed model, of the crystalline nature of the colloidal particles, primarily because we are concerned with the reactions on the surface of the aggregates and in the surrounding solution, which may be supposed to be independent of the detailed core structure except for the fact that such quantities as ion-adsorbing capacities

and dissociating powers of the acidic groups on the surface of the colloidal particles are determined in a fundamental way by the crystalline nature of the particles themselves (Chatterjee, this *Journal, Ind. & News Ed.*, 1949, **12**, 73). The bonding cations become a part of the aggregate itself and are supposed to be immobilised to some extent and replaceable by other cations, whereas the rest are present as free ions in the surrounding solution. Only the latter are capable of registering their activities on suitable measuring devices, e.g. reversible electrodes. The noncrystalline, colloidal ion-exchange resin particles contain bonding cations at an inner surface composed of a covalent hydrocarbon matrix, while the outer surface contributes to free ions. A schematic representation of the proposed model, for example, of a colloidal clay and a colloidally dispersed resin system, is shown in Fig. 1.

FIG. 1



The H^+ ions are present as $(H^+)_i$ in the intermicellar solution and as $(H^+)_a$ in the micellar solution, and the distribution of the cations following addition of reagents is supposed to be guided by the principles of the Donnan equilibrium. A hydrogen electrode, placed in the suspension of a colloidal acid, registers only the active hydrogen ions from the outer surface, *i.e.* those in the intermicellar solution. An alkali, say NaOH, may react in two stages: initially the OH^- ions neutralise the intermicellar or the free H^+ ions, $(H^+)_i$, so that the Na^+ ions become the counter-ions in place of H^+ ions and later on some of those Na^+ ions enter the micellar positions, exchanging with H^+ ions, $(H^+)_a$, in accordance with the laws of the Donnan equilibrium. If a suspension is so visualised that it is devoid of aggregates or inner-surface activity, $(H^+)_a$ are absent and the acid titrates with the characteristic features of a true polybasic acid.

The observed p_H or $(H^+)_i$ is usually referred to the entire volume of the suspension V_s, but since these H^+ ions are present entirely in the volume V_L of the intermicellar solution, the measured H^+ ion activity $(a_H{}^+)_L$ is greater and requires a slight correction for conversion in terms of entire suspension. Since $V_L < V_s$, one gets

$$(a_{H^+})_t = (a_{H^+})_L \times (V_L/V_s)$$

or $$(p_H)_t = (p_H)_L + \log (V_s/V_L) = (p_H)_L + \text{constant},$$

i.e., the corrected neutralisation curve will be slightly raised parallel to that drawn on the basis of observed p_H. As V_L approaches V_s, the difference between the two becomes negligible.

Depending on the relative proportions of the two categories of H^+ ions, three cases may arise, two of which, (A) and (B), refer almost exclusively to either category being present, and the third, (C), to the presence of both categories of H^+ ions.

A. The Hydrogen-ion Activity due to Colloid is present only in the Micellar solution : This is a hypothetical case. The assumption is that there is no contribution to the H^+ ion activity in the intermicellar solution from the surface of the colloidal particles, *i.e.*, the active groups, marked 'a' in Fig 1, are absent. On the addition of an alkali, say NaOH, Na^+ ions take the place of H^+ ions present in the micellar solution, and hence, at any instant of the titration,

$$(a_{H^+})_a + (a_{Na^+})_a = C_a \quad \ldots \quad \ldots \quad (1)$$

where $(a_{H^+})_a$ and $(a_{Na^+})_a$ denote the H^+ and Na^+ activities at any instant and C_a, the initial activity of the H^+ ions in the micellar solution calculated over the whole suspension. Complete neutralisation would mean $C_a = (a_{Na^+})_a$. The total amount 'b' of the added alkali which may be distributed between the two solutions is at any instant given by

$$b = (a_{Na^+})_a + (a_{Na^+})_t \quad \ldots \quad \ldots \quad (2)$$

For electroneutrality in the intermicellar solution

$$(a_{Na^+})_t + (a_{H^+})_t = (a_{OH^-})_t \quad \ldots \quad \ldots \quad (3)$$

Also $$(a_{H^+})_t \times (a_{OH^-})_t = K_w \quad \ldots \quad \ldots \quad (4)$$

where K_w is the ionic product of water.

Applying the Donnan distribution law to each aggregate and summing up for all such aggregates, it can be shown that

$$\frac{(a_{Na^+})_t}{(a_{H^+})_t} = \frac{(a_{Na^+})_a}{(a_{H^+})_a} \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

where all the activities are expressed in g. ions/litre of the suspension.

Putting $x = (a_{H^+})_t$ and substituting the values of the activities in equation (5) from equations (1), (2), (3) and (4) and rearranging, one gets

$$b = (K_w/x) + C_a - x - (C_a.x^2/K_w) \quad \ldots \quad \ldots \quad (6)$$

The curve A corresponding to the above equation is shown in Fig. 2, where $p_H = -\log_{10} x$. Writing equation (6) in terms of p_H, *i.e.*, by replacing x by $(10-p_H)$ and equating (d^2p_H/db^2) to 0, one gets

$$b - C_a = 3.\, C_a.(x^2/K_w)$$

Since (x^2/K_w) is very small at the inflexion point, the corresponding value of 'b' is virtually equal to C_a, the amount of H^+ ions inside the aggregate, which is the total acidity in this case.

B. The Hydrogen-ion Activity due to Colloid is present only in the Intermicellar solution: This case visualises a well-dispersed sol in which the H^+ ions are so disposed with reference to the solid phase that they can freely ionise in the intermicellar solution, *i.e.*, the groups marked 'b' in Fig. 1, are absent. The degree of ionisation will be different at different p_H due to the influence which the size of the colloidal particles, the distance between the ionisable groups and their chemical nature may exert. The polybasicity of the colloidal particles may arise from one or more of these factors. The dissociation constants are therefore likely to have fixed values but may drift in an almost continuous manner as the neutralisation proceeds. For the same type of ionisable groups, the neutralisation curve is expected to be continuous because only when K_{n-1}/K_n is higher than 16, the titration curve with an alkali will show a break (Auerbach and Smolczyk, *Z. physikal. Chem.*, 1924, **110**, 65). This is particularly so when the acidic groups are weakly ionisable. The mathematical treatment becomes complicated in such cases. In a polybasic colloidal acid particle all the ionisable H atoms have equal probability of ionisation, but once one group ionises, the probability is greatest for the remotest hydrogen atom, for the latter will be least influenced by the positive hydrogen ion atmosphere developed surrounding the negative charge. It has been shown (Gane and Ingold, *J. Chem. Soc.*, 1931, 2153) that the ratio K_1/K_2 of dibasic acids of the type $(CH_2)_n(COOH)_2$ decreases from 734 to 7.30 as 'n' increases from 1 to 7. This means that K_2 shows a large proportionate increase as the chain length increases from 2.44 Å, when $n=1$, to 11.79 Å, when $n=7$.

FIG. 2

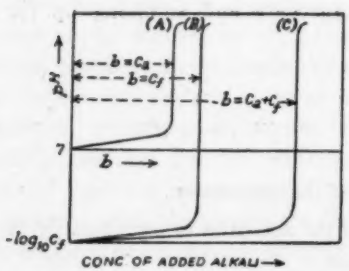
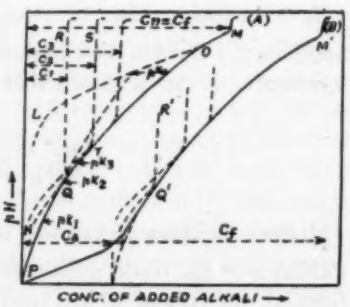


FIG. 3



The distance between ionisable groups on a colloidal acid particle is much more enlarged than what happens on a molecular level, and hence, the ionisation of several acidic groups, separated by quite large distances, on a particular particle, may occur almost independent of one another. Considering all the particles, it is therefore possible to think of a small assembly of ionisable groups constituting a fraction of the total acidity

having dissociation energies not far removed from an average value. In that case the assembly behaves as a monobasic acid of concentration, C_1, and dissociation constant, k_1. A number of such assemblies of ionisable groups may thus be envisaged which differ in their concentration and dissociation constant. Thus, the entire neutralisation curve may be constructed by characterising different stretches of the curve with decreasing dissociation constants k_1, k_2, k_3,...k_n and corresponding monobasic acidities C_1, C_2, C_3...C_n (as shown in curve A of Fig. 3.), where C_n reperesents the total acidity, C_t.

Let the first assembly of acid groups, which can be treated as a monobasic acid, have a concentration, C_1, and a dissociation constant, k_1. Then with reference to the equilibrium $HR \rightleftharpoons H^+ + R^-$

$$(a_{R^-})_f = \frac{C_1 k_1}{k_1 + x} \qquad \ldots \qquad \ldots \quad (7)$$

(by eleminating a_{HR} from the expression for k_1 and the relation $C_1 = a_{R^-} + a_{HR}$). This value of $(a_{R^-})_f$ when introduced in the electroneutrality relation,

$$(a_{Na^+})_f = (a_{OH^-})_f + (a_{R^-})_f - (a_{H^+})_f,$$

one gets

$$b = (K_w/x) + \frac{C_1 k_1}{k_1 + x} - x \qquad \ldots \qquad \ldots \quad (8)$$

Equation (8) (corresponding to FQR) predicts the course of the neutralisation curve up to a certain point (stretch PQ in curve A, Fig. 3). A second similar equation with C_2 and k_2 (curve NQTS) will hold good for the next stretch (QT) and so on. Equation (8) may be analysed further for the case when $b=0$. By neglecting K_w/x, *i.e.* a_{OH^-} in acid solution, one gets

$$X^2 + k_1 X = C_1 k_1 \qquad \ldots \qquad \ldots \quad (9)$$

where X, the initial H^+ ion activity, replaces x. Considering C_1 proportional to the colloid content, 'A', for the same stock suspension, equation (9) becomes $X^2 + k_1 X = \alpha A k_1$, where '$\alpha$' is the proportionality factor. This expresses the variation of H^+ concentration with colloid content. Pallmann (*Koll.- Chem. Beih.*, 1930, **30**, 354), who studied this variation with a number of colloids, obtained linear relationships only at low "relative concentrations". At high "relative concentrations", deviation from linearity was observed by him in the case of a palmitic acid sol and an electrodialysed clay suspension. The above parabolic equation, it will be seen from the data in columns 2, 3, 4 and 5 of Table I(A and B), gives a better fit than Pallmann's linear relationship. The values of C_1 corresponding to relative concentration 100, and k_1 are respectively 2.54×10^{-5} N and 7×10^{-5} for palmitic acid sol and 4.16×10^{-5} N and 20×10^{-5} for the clay suspension (Gupta, *Science & Culture*, 1956, **21**, 547). k_1 for the palmitic acid sol is more or less of the same order as one gets for the first dissociation constant of many polycarboxylic acids in true solution. A similar parabolic curve has been observed in the case of a bentonite suspension by Mukherjee and Mitra (*J. Coll. Sci.*, 1946, **1**, 141), at a low relative concentration.

TABLE I

A. Palmitic acid sol. H^+ ion concentration.				B. Electrodialysed clay suspension. H^+ ion concentration.			
Relative conc.	Obs.	Pallmann.	Calc. from (eq. (9).	Relative. conc.	Obs.	Pallmann.	Calc. from eq. (9),
0	2.07×10^{-6}	1.34×10^{-6}		0.0	2.3×10^{-6}	1.4×10^{-6}	...
10	3.95	3 12	2.5×10^{-6}	9.7	4.9	4.6	$3\,9\times10^{-6}$
25	4.90	5.78	5.9	18.2	6 3	7.4	7.0
40	7.95	8.44	9.0	28.2	9.6	10.7	11.1
50	9 56	10 22	11 0	33.3	11.8	12.5	13.0
75	13.80	14.66	15.6	37.8	13.8	13.9	14.6
100	20.40	19.04	20 1	50.0	19.1	18 0	18.9
200	34.60	35.40	34.2	66 6	25.1	25.6	24 7
300	48.20	54 40	46.1	100	33.9	34 8	35.2
400	56.40	72.10	56.4	200	68.9	68.2	63.2
500	61.40	89.80	65.2	400	108.2	133.9	108.0
600	64.60	107.50	74 1	800	144.6	268 6	176.5
700	68.80	123.90	82.0	Paste	152.6	914 0	...

C. The Hydrogen-ion Activity due to Colloid is present both in the Micellar and in the Intermicellar solution: (*a*). If the ionisable group has a strong acid function, e.g., $-SO_3H$ and $-CH_2SO_3H$, the intermicellar groups, *i.e.*, the groups marked 'a' in Fig. 1, will be all ionised, *i.e.*, $C_i=(a_R^-)_i$. The equation (10) similar to equation (6) may be obtained by evaluating the activities in equation (5). This will simply replace K_w/x term in equation (6) by $(K_w/x) + (a_R^-)_i$, *i.e.*, $(K_w/x) + C_i$.

$$b = C_a + C_i + \frac{K_w}{x} - \frac{C_a\, x}{\frac{K_w}{x} + C_i} - x \qquad \ldots \qquad \ldots \quad (10)$$

The theoretical curve (curve C, Fig.2) resembles features of a strong acid simulating the titration curves of Dowex 50 and Dowex 30 (Tompkins, *J. Chem. Ed.*, 1949, **26**, 35) containing strong acid groups and yet differs from a strong acid (curve B, Fig. 2).

At b=0, neglecting K_w/x, the initial H^+ ion activity $X = C_i$ from equation (10). C_i is, however, a part of the acid representing intermicellar groups only, and therefore the total acidity cannot be calculated from the initial p_H unlike what one gets in the case of a strong acid. At $p_H = 7.0$, $x=K_w/x = 10^{-7}$ one gets from equation (10)

$$b = C_a + C_i - \frac{C_a.\,10^{-7}}{10^{-7} + C_i}.$$

The last term being extremely small, $b = C_a + C_i$, *i.e.*, the amount of alkali required to neutralise the acid at p_H 7.0 is equivalent to both categories of H^+ ions although the initial p_H registered is situated higher than that corresponding to the total acidity.

(*b*). The ionisable groups have a weak acid function, *i.e.* the groups marked 'a' are partially ionised as in Fig. 1, and are neutralised as a polybasic acid, the initial stretch simulating the neutralisation of a monobasic acid, C_1, constituting a fraction of the total acidity, C_i.

The following equation can be derived in which $C_1k_1/(k_1 + x)$ has replaced $(a_{a^-})_f = C_f$ in equation (10).

$$b = C_a + \frac{C_1k_1}{k_1 + x} + \frac{K_w}{x} - \frac{C_a . x}{\frac{C_1k_1}{k_1 + x} + \frac{K_w}{x}} - x \qquad \ldots \quad (11)$$

The theoretical curve PQ'R' for this equation is shown in curve B, Fig. 3., which deviates from the polybasic curve PQ'M' at the point Q' for reasons stated earlier. This type of curve is given by silicic acid sol, colloidal clay acid and some colloidal acid resins. Some of the experimental curves and data, obtained by Mukherjee *et al.* (*Indian J. Agric. Sci.*, 1936, **6**, 517), are shown respectively in Figs. 4-6, and in Table II. They may be analysed as follows. Depending on the method of preparation, silicic acid sol contains a trace of free HCl, estimated quantitatively by ultrafiltration. Accordingly, $(a_{a^-})_f$ has to be corrected for by adding to it the $(a_{Cl^-})_f = r$, say. Moreover, at low p_H, K_w/x may be neglected and equation (11) takes the form (11a).

$$b = C_a + \frac{C_1k_1}{k_1 + x} + r - \frac{C_a . x}{\frac{C_1k_1}{k_1 + x} + r} - x \qquad \ldots \quad (11a)$$

by putting $b = 0$, $x = X$, the initial H^+ ion activity, one gets

$$X = \frac{C_1k_1}{k_1 + X} + r \qquad \ldots \qquad \ldots \quad (11b)$$

The initial p_H of the silicic acid sol, (sol H) and the diluted sols, has been calculated from this relationship and shown in the last column of Table II. Also $C_a + r = 14.4 \times 10^{-5}N$ and $r = 5.0 \times 10^{-5}N$ so that $C_a = 9.4 \times 10^{-5}N$. When the p_H rises by about two units, the last two terms in equation (11a) are of the order of 10^{-7} and can be neglected in comparison to the rest of the terms which are of the order of 10^{-5}. On rearrangement, since $x = X.\ 10^{-\Delta p_H}$, one gets $C_1k_1 = (b - C_a - r)(k_1 + X.\ 10^{-\Delta p_H})$ ... (12)

where Δp_H is the rise in p_H above the initial value.

TABLE II

Conc. of sol in g. mol. of SiO_2/litre = 0.233.

System.	Acid at inflexion.	p_H.	Total Cl^-.	p_H calc. from eq. (11b).
Sol H	$14.4 \times 10^{-5}N$	4.10 (Quinhydrone) 4.02 ($Pt—H_2$)	$5.0 \times 10^{-5}.N$	4.24
Sol H/2	7.2	4.30 (Quinhydrone) 4.16 ($Pt—H_2$)		4.50
Sol H/5	3.1	4.60 (Quinhydrone) 4.09 ($Pt—H_2$)		4.82
Sol H/10	1.6	4.67 (Quinhydrone) 4.14 ($Pt—H_2$)		5.03
Sol H/20	0.8	4.91 (Quinhydrone) 5.09 ($Pt—H_2$)		5.24
Ultrafiltrate of Sol H*			5.0	

k_1 may be solved in terms of X by considering two successive values of C_1k_1, treating it as a constant over the range. These calculations are shown in Table III.

TABLE III

Δp_H.	Conc. of alkali added ($b \times 10^5$).	$C_1k_1 \times 10^5$.	k_1.
1.5	32.5	18.1 (k_1 + 0.03162 X)	0 0085 X
1.6	36.0	21.6 (k_1 + 0.02572 X)	0.0084 X
1.7	40 0	25.6 (k_1 + 0.01995 X)	0.0075 X
1.8	44.5	30.1 (k_1 + 0.01585 X)	

Taking k_1 = 0.0084. X, C_1 becomes equal to 86.4 × 10^{-5} using equation (12). From equation (11b), $X = 5.725 \times 10^{-5}$ corresponding to p_H 4.24. Hence, $k_1 = 4.809 \times 10^{-7}$. Inserting these values in equation (11a), the theoretical titration curve for silicic acid sol H is obtained and compared with the experimental one in Fig. 4. The curve for sol H/2, also shown in Fig. 4, has been constructed keeping k_1 constant with the values of C_a, r and C_1 exactly halved. The curve for the third sol, sol H/5, (Fig. 5), necessitates calculations of C_2 and k_2 for streches beyond C_1 from the slope of the curve and are found to be 262 × 10^{-5} and 8.03 × 10^{-8} respectively. For the construction of curves for sol H/10 and sol H/20, shown in Fig. 6, the initial stretches have been computed by using proper fractions of C_1 and C_2 together with the dissociation constants, k_1 and k_2. For the construction of stretches beyond C_2, a third dissociation constant k_3 (2.6 × 10^{-8}) and acidity C_3 (546 × 10^{-5}) have been used.

FIG. 4

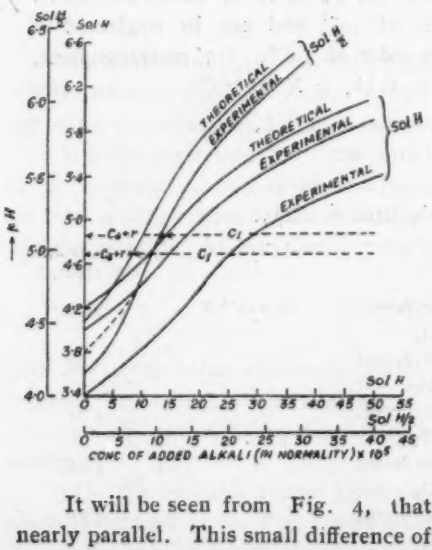
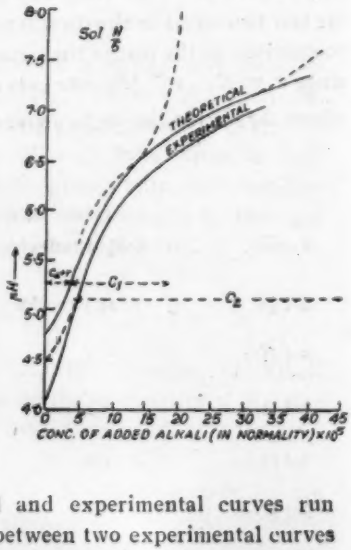


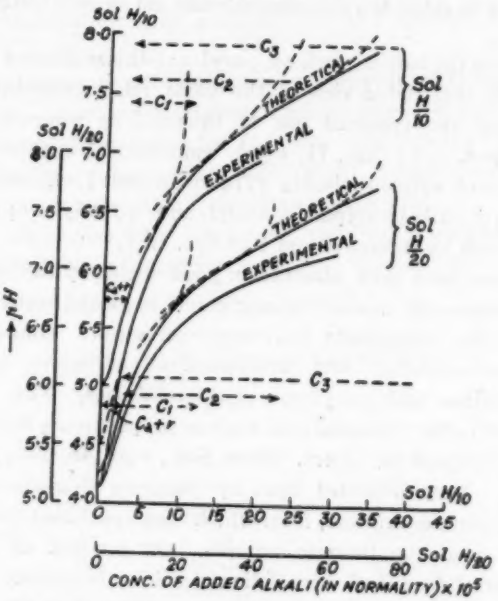
FIG. 5



It will be seen from Fig. 4, that the theoretical and experimental curves run nearly parallel. This small difference often occurs even between two experimental curves for the same sol, as shown by the two experimental curves for sol H. The dotted lines

with the experimental curves for sol H/2, sol H/5 and sol H/10 show what could have been a better fit. The deviation may be due to contamination of KCl from the ground-in glass junction of the salt bridge, as a result of which H^+ ions are likely to be exchanged and released from $(H^+)_a$ by K^+ ions, indicating a lower p_H.

FIG. 6



It is an experimental fact that the potentiometric titration curves of silicic acid sols and clay acids show different features depending upon the nature of the cation of the base used to titrate them. Thus, while NaOH and KOH show a weak acid feature, $Ca(OH)_2$ and $Ba(OH)_2$ suggest strong acid features. On the basis of the double layer theory, the discrepancy has been explained by the fact that the bivalent cations are more strongly adsorbed and form ion-pairs; consequently they show greater buffering characteristic of strong acids. According to the picture presented here, we would say, that the bivalent cations increase aggregation as they are definitely known to do so, and thereby increase the value of C_a, and according to case A, this will impart a strong acid character to the system. This idea may easily be extended to understand the higher observed acidity of the colloidal acids when titrated with bases in presence of neutral salts than when titrated alone. A quantitative treatment of these cases requires a more definite knowledge of the aggregates than what is available at present. In our next communication we will deal with some clay acid titrations in the light of the above formulations.

The author's thanks are due to Dr. S. K. Mukherjee, Lecturer in the Applied Chemistry Department, Calcutta University, for helpful criticisms and encouragement.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY COLLEGE OF SCIENCE
& TECHNOLOGY, CALCUTTA.

Received September 22, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 8, 1956]

STUDIES ON 3-*o*-TOLYL- AND 3-*p*-TOLYL-2 : 4-THIAZOLIDIONES

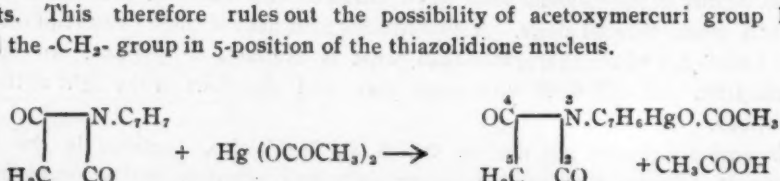
By P. N. Bhargava, R. P. Rao and M. S. Sastry

3-*o*-Tolyl- and 3-*p*-tolyl-2 : 4-thiazolidiones have been synthesised by condensing the corresponding *S*-di-*o*-tolyl- and *S*-di-*p*-tolylthioureas with monochloroacetic acid in glacial acetic acid medium, and their various derivatives with aldehydes, diazonium chlorides and mercuric acetate have been prepared.

In continuation to the earlier work on 3-aryl-2 : 4-thiazolidiones (Bhargava and Rao, this *Journal*, 1955, **32**, 463) and in view of the close relationship between thiazolidiones and thiazolidones and the reported use of thiazolidone compounds as anaesthetics (Surrey, *J. Amer. Chem. Soc.*, 1949, **71**, 3354), amoebacidal agents (Surrey and Cutler, *ibid.*, 1954, **76**, 578) and anticonvulsants (Troutman and Long, *ibid.*, 1948, **70**, 3436), it was considered worthwhile to prepare 3-*o*-tolyl- and 3-*p*-tolyl-2 : 4-thiazolidiones under the conditions laid down by Bhargava and Rao (*loc. cit.*).

The thiazolidiones have been obtained in good yields by the interaction of *S*-di-*p*- and *S*-di-*o*-tolylthioureas with monochloroacetic acid in glacial acetic acid. The reactive methylene group of the compounds has been successfully condensed with aromatic aldehydes, α-nitroso-β-naphthol and aryldiazonium chlorides, forming respectively 5-arylidene-, 5-arylimino- and 5-arylazo-2 : 4-thiazolidiones. The assumption that the azo group is attached to the thiazolidione nucleus in position-5 is based on the observations of Bogert and Chertcoff (*J. Amer. Chem. Soc.*, 1924, **46**, 2864 ; *Proc. Nat. Acad. Sci.*, 1924, **10**, 418). They obtained dyes by coupling diazotised *p*-nitroaniline and sulphanilic acid with 2-aminothiazole, from which they concluded that the azo group was attached to position-5 of the thiazole nucleus. On account of a close relationship among thiazole, thiazolidone and thiazolidione, similar behaviour is also expected of thiazolidiones. Meerwein, Buchner and Engster (*J. parkt. Chem.*, 1939, **152**, 237) studied the reactions of diazonium salts with αβ-unsaturated carbonyl compounds and concluded that the arylazo group entered the position α to the activating carbonyl group. Hence, the attachment of the azo group to $-CH_2-$ group in position-5 in α-position to the activating carbonyl group is justified and is further supported by the observation that when the $-CH_2-$ group in position-5 of the thiazolidione nucleus is blocked by condensation with aromatic aldehydes, no azo dye is formed.

Further, mercuration of 3-*p*-tolyl-2 : 4-thiazolidione (I) with mercuric acetate has yielded 3-acetoxymercuri-*p*-tolyl-2 : 4-thiazolidione (II). The acetoxymercuri group is assumed to enter the aryl nucleus in view of the fact that the 3-*o*-tolyl-2 : 4-thiazolidione derivatives are mercurated under similar conditions giving rise to exactly similar products. This therefore rules out the possibility of acetoxymercuri group having entered the $-CH_2-$ group in 5-position of the thiazolidione nucleus.



(I) (II)

EXPERIMENTAL

3-p-*Tolyl* - 2 : 4 - *thiazolidione* was prepared according to the method of Klare, Markley and Reid (*J. Amer. Chem. Soc.*, 1930, **52**, 2137) in glacial acetic acid or alcohol along with HCl (conc.) in white needles, m.p. 162°. (Found : S, 15.54. $C_{10}H_9O_2NS$ requires S, 15.49 per cent).

3-o-*Tolyl*-2 : 4-*thiazolidione* was prepared by the method of Bhargava and Rao (*loc. cit.*), m.p. 154°.

3-o-*Tolyl*-5-*benzylidene*-2 : 4-*thiazolidione*.—A mixture of thiazolidione (0.5 g.) and benzaldehyde (0.3 g.), dissolved in glacial acetic acid (10 c.c.), and fused sodium acetate (1 g.) was heated under reflux for 1½ hours. On pouring the contents into water a precipitate was obtained. After keeping it overnight, the yellow precipitate was filtered off and the product was recrystallised from glacial acetic acid.

Similarly other aldehydes were condensed yielding 5-arylidene derivatives. The properties and analytical data of these derivatives are recorded in Table I.

TABLE I

3-o-*Tolyl*-5-*arylidene*-2 : 4-*thiazolidione*.

Aldehyde.	% Yield.	Colour.	M.P.	% Sulphur. Found.	Calc.
Benzaldehyde	72	Deep yellow	133-35°	10.86	10.84
m-Nitrobenzaldehyde	66	Yellow	156°	9.62	9.41
m-Hydroxybenzaldehyde	75	Light yellow	160°	10.38	10.30
p-Hydroxybenzaldehyde	70	Do	168-70	10 41	10.30
Cinnamaldehyde	60	Yellowish brown	98° (decomp.)		
Furfuraldehyde	55	Greyish brown	101°	11.03	11.22

3-p-*Tolyl*-5-*benzylidene*-2 : 4-*thiazolidione* was prepared according to the above method, and similarly other aldehydes and α-nitroso-β-naphthol were also condensed with the thiazolidione. The products and their analytical data are noted in Table II.

TABLE II

3-p-*Tolyl*-5-*arylidene*- *and* -5-*arylimino*-2 : 4-*thiazolidiones*.

Aldehydes or nitroso compound.	% Yield.	Colour.	M.P.	% Sulphur. Found.	Calc.
Benzaldehyde	70	Pale yellow	208°	10.80	10.84
o-Nitrobenzaldehyde	80	Yellow	224°	9.46	9.41
m-Nitrobenzaldehyde	50	Do	216°	9.42	9.41
m-Hydroxybenzaldehyde	82	Pale yellow	222°	10.21	10.30
Salicylaldehyde	62	Do	242°	10.34	10.30
Anisaldehyde	53	Yellow	204°	9.90	9.86
p-Dimethylaminobenzaldehyde	67	Orange	236°	9.47	9.49
Cinnamaldehyde	45	Yellow	201°	9.94	9.98
Vanillin	77	Do	235°	9.37	9.39
Veratraldehyde	84	Pale yellow	194°	8.99	9.03
Piperonal	91	Do	220°	9.42	9.45
α-Nitroso-β-naphthol	71	Brown	205°	8.82	8.85

3-o-*Tolyl*-5-*phenylazo*-2 : 4-*thiazolidione* was prepared by the method of Bhargava and Goswami (this *Journal*, 1955, **32**, 763). Similarly the thiazolidione was condensed with a number of aryldiazonium chlorides. The properties of these compounds and their analytical data are recorded in Table III.

TABLE III

Diazonium chloride of amines.	Colour.	M.P.	% Sulphur. Found.	Calc.
Aniline	Yellow	148°	10.37	10.30
o-Toluidine	Dirty yellow	136°	9.86	9.84
p-Toludine	Light yellow	146°	10.01	9.84
α-Naphthylamine	Dark brown	119°	8.82	8.86
β-Naphthylamine	Scarlet-red	113-15°	8.87	8.86
p-Anisidine	Ash-grey	145°	8.32	8.38
Sulphanilamide	Deep yellow	120-22°	16.36	16.41

Similarly 5-arylazo derivatives of 3-*p*-tolyl-2 : 4-thiazolidione were prepared (Table IV).

TABLE IV

Diazonium chloride of amines.	Colour.	M.P.	% Sulphur. Found.	Calc.
Aniline	Brown	130°	10.34	10.30
p-Toluidine	Orange-red	195°	9.81	9.84
Sulphanilamide	Scarlet-red	>300°	16.36	16.41

3-*Acetoxymercuri*-p-*tolyl*-2 : 4-*thiazolidione*.—3-*p*-Tolyl-2 : 4-thiazolidione (1 g.) was dissolved in glacial acetic acid (20 c.c.) and to this absolute alcohol (15 c.c.) and mercuric acetate (1.5 g.), dissolved in water (15 c.c.) and acidified with acetic acid, were added. On keeping overnight, a precipitate was obtained, which was filtered, washed respectively with dilute acetic acid, hot water and alcohol. It was crystallised from alcohol in a pale yellow form, m. p. 310°. (Found : Hg, 42.81. $C_{12}H_{11}O_4NSHg$ requires Hg, 43.08 per cent).

3-*Acetoxymercuri*-o-*tolyl*-5-*benzylidene* 2 : 4-*thiazolidione* was prepared by the above method by mercurating 3-o-tolyl-5-benzylidene-2 : 4-thiazolidione and was obtained in a yellowish white form, m.p. 170-71°. (Found : Hg, 36.66. $C_{19}H_{15}O_4NSHg$ requires Hg, 36.49 per cent).

The presence of one acetoxymercuri group in this compound and in 3-acetoxymercuri-*o*-tolyl-2 : 4-thiazolidione (Bhargava and Rao, *loc.cit.*) as well as in 3-acetoxymercuri-*p*-tolyl-2 : 4-thiazolidione clearly indicates that the acetoxymercuri group has entered the aryl nucleus at position-3 and not the methylene group at position 5.

Thanks are due to the authorities of the Banaras Hindu University for providing facilities in the Organic Chemical Laboratory.

ORGANIC CHEMICAL LABORATORY,
COLLEGE OF SCIENCE,
BANARAS HINDU UNIVERSITY.

Received March 3, 1956

[Jour. Indian Chem. Soc., Vol. 33, No. 8, 1956]

ABSORPTION AND FLUORESCENCE SPECTRA OF CHROMONES

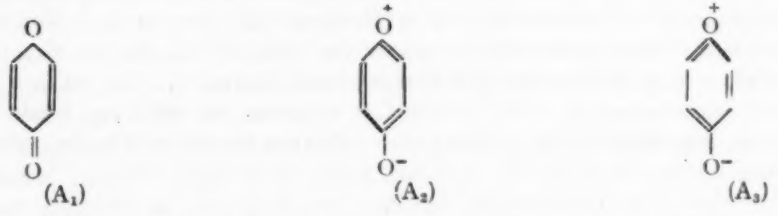
By S. K. K. Jatkar and B. N. Mattoo

Absorption and fluorescence spectra of 7-hydroxy-2-methyl-, 7-hydroxy-2-methyl-3-acetyl-, 7-acetoxy-2-methyl, 7-methoxy-2-methyl-, 5-hydroxy-2-methyl-chromones have been studied. Absorption spectrum of chromone is modified by introduction of hydroxyls, which make additional resonance possible (e.g. 5-OH; 7-OH derivatives). Etherification of 7-OH does not change the nature of absorption. Acetylation reverts the spectrum to that of chromone without any hydroxyl. Fluorescence is exhibited only by 7-hydroxychromonone. Chelation (5-OH deriv.) results in complete inhibition of fluorescence.

Absorption spectra of γ-pyrone and chromone have been reported by Gibbs *et al.* (*J. Amer. Chem. Soc.*, 1930, **52**, 4895). The former exhibits a maximum at $\sim 40.7 \times 10^3$ cm^{-1} (250mμ region) with fine structure on low-frequency side, viz., at 39.3×10^3 cm^{-1} and 38.4×10^3 cm^{-1}. Chromone has been shown to have two bands, one resolved into two adjacent bands of the same ε at 33.2×10^3 cm^{-1} and 33.8×10^3 cm^{-1} (301, 296mμ) and another at 42.2×10^3 cm^{-1} (237mμ), with ε values of 7.9×10^3 and 10.5×10^3 respectively.

According to Aronoff (*J. Org. Chem.*, 1940, **5**, 561) γ-pyrone has another band in 200 mμ region. Chromone, he reports, exhibits in addition to the two γ-pyrone maxima, viz. 200 and 250 mμ, a third at 300 mμ. Mentzer and Meunier (*Bull. soc. chim.*, 1944, **11**, 302) have reported the spectra in EtOH of 3-methylchromone and 3-ethyl-6-methyl derivative. Other absorption spectra data for various chromone derivatives have been reported by organic chemists (Schmutz, *Helv. Chim. Acta*, 1951, **34**, 767; Bolleter, *ibid.*, 1951, **34**, 186).

Berson's qualitative interpretation (*J. Amer. Chem. Soc.*, 1953, **75**, 3521) of the absorption of pyrones and benzopyrones includes the following resonance structures for γ-pyrone :



According to Berson, the Kekule heteropolar structures, A_2 and A_3, make significant contribution in the first excited state. Inclusion of 'intermediate' dipolar structures is important because the probability of direct transition from structure A_1 to the extreme heteropolar structures A_2, A_3 is very small. Only small contribution is made by dipolar structures in the ground state of chromone (cf. LeFevre, *J. Chem. Soc.*, 1937, 196).

There are no quantitative measurements on fluorescence spectra of chromones, reported so far. Seshadri *et al.* (*Proc. Ind. Acad. Sci.*, 1940, **12A**, 375; 1951, **34A**, 319)

have qualitatively studied the fluorescence of chromone derivatives in the light of chemical constitution. Their work consists in visual examination of fluorescence excited by daylight. In their discussions no regard has been taken of the exciting radiation. The concentration range at which the observations have been made are not reported. Due to concentration quenching, erroneous observations could have easily been made.

These authors have studied the effect of acid, alkali and various substitutions on the fluorescence of chromone nucleus. The data are represented graphically in Figs. 1-4.

Absorption

The characteristic chromone spectrum (two bands at 2,500 and 3,000Å) is modified by introduction of hydroxyl groups, their methyl ethers and other substituents, and this is found to be due to the possibility of additional resonances over and above that in the chromone structure. The presence of a 2-Me group in the hydroxychromones, studied here, can reasonably be assumed to have little effect on absorption excepting a very minor hyperconjugative effect of $-CH_3$.

7-OH group in 2-methylchromone modifies the chromone spectrum radically, giving rise to absorption bands at 216, 248 (fine structure), and 294 mμ with extinction coefficients of 20800, 19,550 and 11,900 respectively.

The additional resonance possible with this group is similar to that suggested by Aronoff for 7-hydroxyflavone (*loc. cit.*):

Considering the normal resonance, the higher dipole strength of transition, as compared to that of the corresponding α-pyrones (coumarins), gives rise to comparatively high integrated absorption. $\int \varepsilon d\nu$ for 4-methyl-7-hydroxycoumarin and 2-methyl-7-hydroxychromone in neutral solution is 36.2 and 52.4 respectively. The oscillator strength of the longest-wave band (294 mμ) of the latter is also higher, viz., 0.28, as compared to 0.23 for the corresponding α-pyrone derivative. In alkaline ($10^{-4}N$) medium, where ionisation of the hydroxyl is increased, an additional band, removed to the red, is produced at 338 mμ ($\varepsilon = 5{,}180$). This can be attributed to the resonance of the type:

in the ionic state. A 5-OH group in 2-methylchromone also influences the absoption spectrum, due to the possibility of the additional resonance of the type:

Now the absorption bands lie at 325, 252, 233 and 226.5 mμ with ε=4,730; 13,550; 20,750 and 20,500 respectively. The oscillator strengths of the bands at 325 and 252 mμ are 0.09 and 0.21 respectively.

There is, however, no change in spectrum with p_H. This can be attributed to the inhibition of the ionisation of the hydroxyl at 5-position, because of strong chelation, as already reported by Simpson and Garden (*J. Chem. Soc.*, 1952, 4638) from chromatographic study.

The methylation of the hydroxyl at 7-position retains the nature of absorption spectrum completely, because even now the additional resonance, as with 7-OH, is possible. There being no ionisation now, the p_H-dependence of the spectra as well as the additional long-wave band characteristic of the ionic form is absent. Methylation shifts the absorption slightly to shorter wave-length but increases ε and $\int \varepsilon dv$. The oscillator strength of the longest-wave band of 7-methoxy-2-methylchromone (292 mμ) is 0.30 as compared to 0.28 of the 294 mμ band of the 7-OH analogue.

Acetylation of the hydroxyl at 7-position reverts the spectrum to that of chromone. This is obviously due to the fact that the additional resonance possible with -OH is inhibited by its conversion into $-O.CO.CH_3$.

Introduction of a 3-acetyl group in 7-hydroxy-2-methylchromone, though retains the spectral character of absorption in the longest-wave band yet there is a radical change in the spectrum in the shorter wave-length side. The bands now lie at 295 and 249 mμ with minima at 275 and 220 mμ. With this acetyl group the additional resonance due to -OH is not affected; however, the normal resonance in chromone nucleus is affected. The 'additional' resonance, which is more important in hydroxy compounds, being unaffected, we observe that the introduction of acetyl group at 3-position does not produce such a radical change in the absorption of the corresponding -OH compound, as when the acetyl group is at a position *ortho* to the hydroxyl (e.g., 8-acetylumbelliferone, work under publication).

The dependence of spectrum of 3-acetyl-2-methyl-7-hydroxychromone on p_H and exhibition of isobestic points is, of course, expected. The integrated absorption of this compound is slightly greater than that of 2-methyl-7-hydroxychromone: $\int \varepsilon\, dv = 53.7$ and 52.4 respectively, for neutral solutions.

Fluorescence

Amongst the few chromones available for this study, 7-hydroxy-2-methylchromone only exhibited a fluorescence emission comparable in intensity with the corresponding α-pyrones. The other derivatives had very low fluorescence, so as not to enable the authors to determine the fluorescence spectrum, though the approximate values of F_{max} were determined in each case. 7-Hydroxy-2-methylchromone shows blue fluorescence

FIG. 1

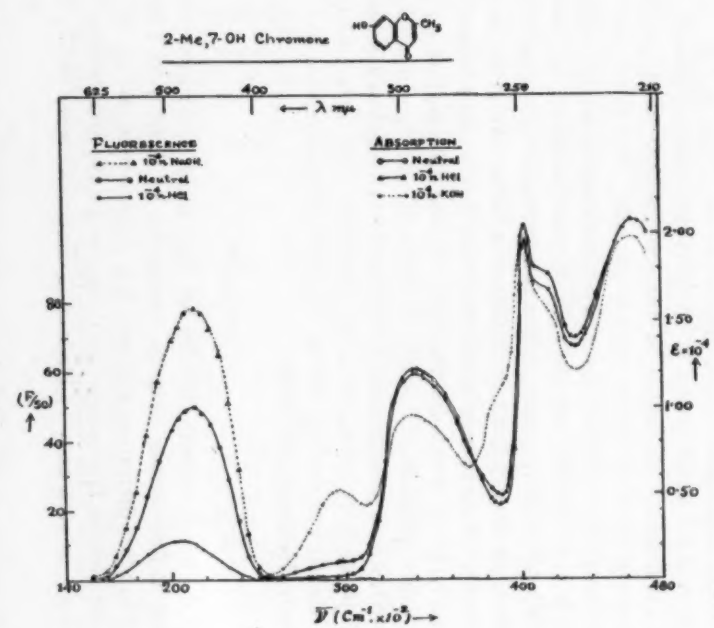
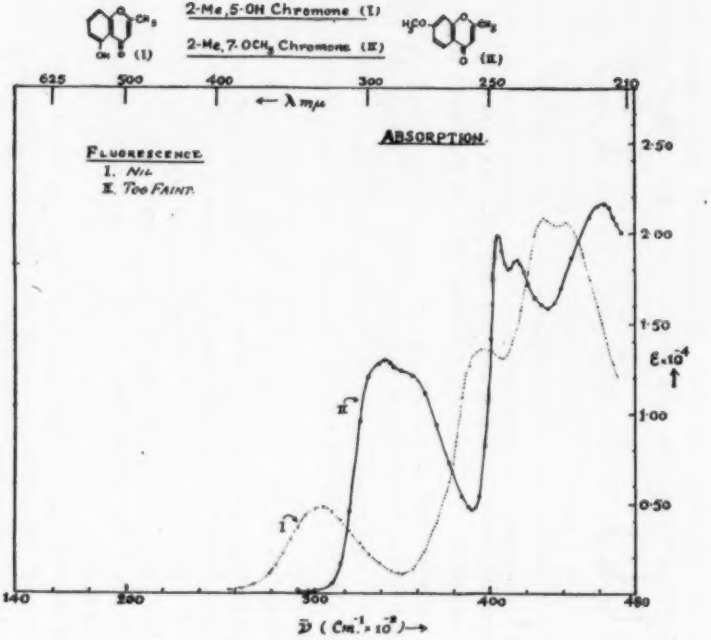

2-Me, 7-OH Chromone
Fluorescence
10⁻³% NaOH
Neutral
10⁻⁴% HCl
Absorption
Neutral
10⁻³% HCl
10⁻³% KOH
λ mμ
625 500 400 300 250 210
(F/50)
ε×10⁻⁴
2·00
1·50
1·00
0·50
140 200 300 400 480
ν̄ (Cm⁻¹ x10⁻³)

FIG. 2


2-Me, 5-OH Chromone (I)
2-Me, 7-OCH₃ Chromone (II)
(I)
(II)
λ mμ
625 500 400 300 250 210
Fluorescence
I. Nil.
II. Too Faint.
Absorption
II
I
ε×10⁻⁴
2·50
2·00
1·50
1·00
0·50
140 200 300 400 480
ν̄ (Cm⁻¹ x10⁻³)

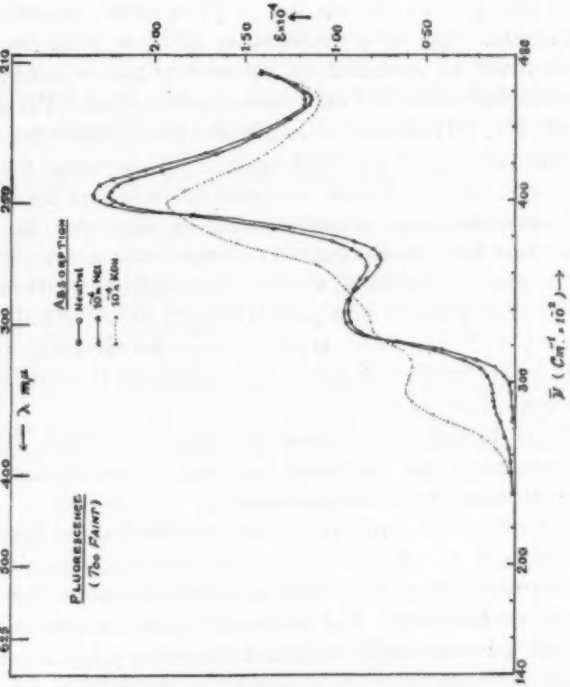

2-Me, 3-Acetyl, 7-OH Chromone
Absorption
Neutral
10⁻⁴ N HCl
10⁻⁴ N KOH
Fluorescence (Too Faint)
λ mμ
ν̄ (Cm⁻¹ · 10⁻³) →
ε × 10⁻⁴

FIG. 4

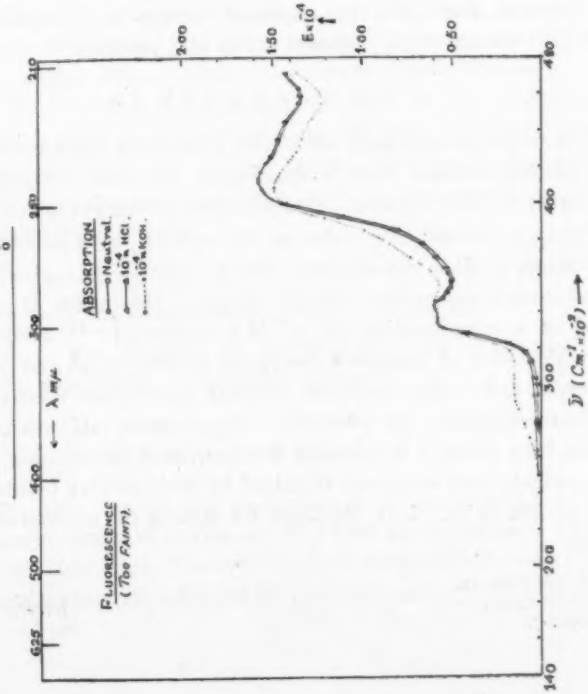

7-Acetoxy Chromone
Absorption
Neutral
10⁻⁴ N HCl
10⁻⁴ N KOH
Fluorescence (Too Faint)
λ mμ
ν̄ (Cm⁻¹ · 10⁻³) →
ε × 10⁻⁴

FIG. 3

with maxima at 470, 470 and 485 mμ for $10^{-4}N$ alkaline, neutral, and $10^{-4}N$ acidic solutions respectively. The total fluorescence, $\int Fdv$, in these media is 10,250, 6,050 and 1,350 respectively as compared to values of 13,500, 10,500 and 8,400 respectively, for 7-hydroxy-4-methylcoumarin (work under publication). The increase in resonance on introduction of 7-OH should be responsible for its fluorescing property. As found in coumarins, the ionic form of 7-hydroxy-2-methylchromone has also much greater quantum efficiency, and the fluorescence band for ionic form lies at shorter wave-length than that of the molecular form, notwithstanding the fact that the ionic form has an additional absorption band, much removed to longer wave-length.

Although resonance is increased with an introduction of 5-OH in 2-methylchromone, the inhibition of fluorescence is most probably due to strong chelation of this hydroxyl with the carbonyl of the γ-pyrone. However, there are exceptions to this generalisation of inhibition of fluorescence by chelation, e.g. quinizarin (Bowen and Wokes, "Fluorescence of Solutions", Longmans, 1953).

Acetylation of the hydroxyl at 7-position renders this group ineffective to produce the additional resonance and the behaviour is more or less the same as that of chromone without -OH substituent; hence no fluorescence.

The etherification of the hydroxyl at 7-position inhibits the fluorescence, F_{max} being now ~5 as compared to 2,510 for 7 hydroxy-2-methylchromone in neutral solution. Introduction of 3-acetyl group in 7-hydroxy-2-methylchromone also results in a great set-back in quantum efficiency. The values of F_{max} now, are 25, 10 and ~0 for alkaline, neutral and acidic solutions respectively, as compared to 3,925, 2,510 and 565 respectively when there is no acetyl group. The chromone resonance being affected by this group, the normal electron drift from the anionoid oxygen at 1 to cationoid oxygen at 4 is hampered by the presence of the carbonyl group at 3-position.

EXPERIMENTAL

Absorption measurements were made with a Beckman DU spectrophotometer and the fluorescence spectra obtained with a fluorimeter assembly consisting of a hydrogen discharge (source), a Fuess constant-deviation spectroscope as the dispersing element, and an IP28 photoelectron-multiplier tube at the exit slit, with an additional amplifier (cf. Jatkar and Mattoo, *J. Univ. Poona*, 1954, No. 6, 67).

The solvent used was aqueous alcohol (87%). Absorption as well as fluorescence were studied at a concentration of $10^{-4}M$ in neutral, $10^{-4}N$ acidic and $10^{-4}N$ alkaline media. For calculation of integrated absorption (limits 2,100Å and 5,000Å) and fluorescence, the areas under the respective spectral curves (on wave-number scale) were measured planimetrically. In comparing fluorescence efficiencies qualitatively, no cognizance has been taken of the spectral distribution of the exciting source.

The compounds used were pure as judged by their melting points.

Thanks are due to Dr. M. G. Marathey for making the compounds available for the present study.

CHEMISTRY DEPARTMENT,
POONA UNIVERSITY,
POONA-7.

Received November, 8, 1955.

[Jour. Indian Chem. Soc., Vol 33, No. 8, 1956]

ANODIC PHENOMENA IN THE ELECTROLYSIS OF SILVER SALTS. PART I. FORMATION OF SILVER PEROXYNITRATE

By A. N. Kappanna and Indra Dev Arya

A study has been made of the phenomena at the anode when aqueous silver nitrate solutions are electrolysed between platinum and gold electrodes under different current-potential conditions.

Decomposition and anode discharge potentials have been determined for solutions of different concentrations, both in neutral and acid solutions, and at different temperatures. Current-potential curves are quite smooth and continuous in all cases.

The results of the analysis of the anodic product, prepared under a variety of conditions, show that it has, whenever formed, the same composition corresponding to the formula $Ag_7O_8.NO_3$.

The following mechanism is suggested for the formation of the peroxynitrate. The nitrate radicals liberated on the anode immediately react with silver ions to form simultaneously Ag^{2+} and Ag^{3+}. This is quickly followed by $Ag^{2+} + H_2O \rightarrow AgO + 2H^+$ and $2Ag^{3+} + 3H_2O \rightarrow Ag_2O_3 + 6H^+$, and AgO with Ag_2O_3 forming a complex $AgO.Ag_2O_3$ and then two of the complexes $AgO.Ag_2O_3$ imbibing one molecule of $AgNO_3$ to form $Ag_6O_8.AgNO_3$ or $Ag_7O_8.NO_3$.

The brownish black crystalline product, formed on a platinum anode during the electrolysis of silver nitrate, is commonly referred to as silver peroxynitrate. The composition of the product has been the subject of numerous investigations. There appears to be a good measure of agreement that its composition corresponds to $Ag_7O_8.NO_3$. Noyes *et al.* (*J. Amer. Chem. Soc.*, 1937, **59**, 1326) were able to show that this product was formed on the anode even in the presence of free nitric acid in the solution. An extraordinary observation made by Kappanna and Talati (this *Journal*, 1951, **28**, 417) that a paramagnetic oxide of the composition AgO_2 is formed at the anode in the electrolysis of silver fluoride solutions, has stimulated further investigations on anodic phenomena in the electrolysis of silver salts in this laboratory. The present communication deals with the results of an investigation undertaken to determine the following :

1. The current potential conditions for the formation of peroxynitrate.
2. The composition of the product under different conditions.
3. The influence of the presence of acetone and alcohol in the electrolyte on the formation and composition of the anodic product.

Experimental

The experiments were carried out in beakers of 250 c.c. capacity, using platinum electrodes ; a few experiments were carried out with gold electrodes also. The electrolyte, silver nitrate solution, was kept stirred by an electrically driven stirrer. Current was drawn from lead accumulators and regulated by rheostats, micro or milliammeters having been included in the circuit.

Decomposition and discharge potentials were measured with the aid of a precision potentiometer. A saturated calomel element with saturated ammonium nitrate bridge was used as a reference electrode for single electrode potential measurements.

Table I shows the decomposition and anode discharge potentials of solutions of different concentrations at different temperatures. The anode potentials are with reference to hydrogen electrode zero.

TABLE I

Solutions.	Temp.	Decomp. potential.	Anode discharge potential.
N-$AgNO_3$	25°	0.715	1.476
	50°	0.706	1.446
	60°	0.700	1.426
	70°	0.690	1.326
$N/10$-$AgNO_3$	25°	0.765	1 486
	50°	0.725	1.446
	60°	0.680	1.406
	70°	0.625	1.364
$N/5$-$AgNO_3$ + $N/5$-HNO_3	25°	0.975	1.656
$N/20$-$AgNO_3$ + $N/20$-HNO_3	25°	0.950	1.656
$N/40$ $AgNO_3$ + $N/10$-HNO_3	25°	0.925	1.626

It will be observed that decomposition potentials and anode discharge potentials fall with increase in temperature. The addition of free nitric acid raises both these properties. The decomposition and discharge potential curves were in all cases found to be continuous and smooth and did not reveal any abnormality, indicating that the reactions on the anode were purely secondary, following the primary discharge of nitrate ion. Detailed and repeated studies were made to see if any breaks, either in the impressed current-potential or anode current-potential curves, above the decomposition potential or anode discharge potential, could be observed with a view to determining any particular current density or potential at which the anodic deposition of the complex compound commenced, but without any tangible result. Close observations were next made just at the discharge potential point, maintaining the current and potential constant. The current passed in several cases was very small, in the neighbourhood of 30-50 microamperes. The chemical effects at the anode were sufficiently slow and could be followed visually. The bright platinum anodes first turned dull and then slightly yellowish. The yellow gradually turned into red, brown and brownish black. The change in colour is in all probability due to change in the size of the crystals and the thickness of the deposit.

Preparation and Analysis of the Product.—The appearance of the product depended upon the current density. At comparatively low current densities, the deposit looked smooth and uniform. At higher current densities, the crystals grew in size rapidly and the tendency to grow into long needles at certain places in preference to others was observable. In all cases the deposit was beautifully crystalline and adherent. It was only at later stages, when the needle-like crystals became sufficiently long, that any tendency to fall off from the electrode became noticeable.

The formation of peroxynitrate is accompanied by the liberation of nitric acid in the neighbourhood of the anode, and free acid lowers the efficiency of the formation of the anodic deposit. It was therefore found necessary, in order to obtain better yields, to keep freshly precipitated silver carbonate in a filter paper bag inserted in a perforated test tube, inside the electrolytic cell to maintain the solution neutral. A comparative idea of the yields under different conditions can be had from Table II. The experiments were all performed at the room temperature (30-31°).

TABLE II

Conc. of $AgNO_3$.	Current density.	Amp. hrs passed.	Wt. of deposit.	Remarks.
N/10	5.6 milliamps.	0.060	0.0184 g.	
"	13.5	0.1833	0.2044	Brisk evolution of O_2 after 2½ hours.
0.5N	140	1.0	1.7088	Do after 1 hour.
N	140	1.0	2.6430	
N	110	1.0	3.4080	Silver carbonate in the filter paper bag.
N- at 0°	110	1.0	3.2250	Do
N- at 75°	110	1.0	1.3800	Do
N- at 30°	110 (gold electrodes)	1.0	2.1314	

The results in Table II indicate clearly that the current efficiency is dependent on : (*i*) current density, increasing with increase in current density ; (*ii*) concentration of silver ion in solution, increasing with increase in concentration ; (*iii*) it is practically independent of temperature between 0° and 30°, while at higher temperatures, as found at 75°, it diminishes considerably ; and (*iv*) on the neutrality of the solution, being considerably enhanced by the solution being maintained neutral by the suspension of silver carbonate.

Composition of the Compound.—Earlier workers* including Noyes *et al.* (*loc. cit.*) attributed the formula $Ag_7O_8.NO_3$ to the complex formed on the anode. In the present investigation, the analysis of the compound prepared under different conditions has been carried out for the percentages of sliver, NO_3 radical and available oxygen.

Silver was estimated volumetrically by the thiocyanate method. Available oxygen was determined by reduction with ferrous sulphate in acid (H_2SO_4) solution. Nitrate was estimated as nitron nitrate after decomposition of the compound with boiling H_2SO_4 (dil.). Table III records the results of analysis.

TABLE III

Sample (Table II) ...	1	2	3	4	5	7	8	$Ag_7O_8NN_2$
Ag (%) ...	80.13	79.90	79.70	79.20	79.40	80.01	79.10	79.91
**Available oxygen (%)	...	...	8.11	7.80	7.43	7.66		8.456
NO_3 (%) ...			6.90	7.02	6.85	6.95		6.554

*References to earlier workers are to be found in the papers by Noyes *et al.*

**At the suggestion of the Editor the percentage of available oxgen was determined by the iodide oxidation method (estimating the liberated iodine) in dilute sulphuric acid solutions. Practically identical values were obtained.

These results definitely indicate that the composition of the anodic product formed under a variety of conditions is practically the same. Further, the analytical figures lend support to the formula $Ag_7O_8.NO_3$, suggested by earlier workers.

Influence of Alcohol and Acetone.—Alcohol and acetone are good solvents for silver nitrate, and observations regarding anodic reactions in the electrolysis of this electrolyte in these solvents have not been recorded in literature. Experiments were therefore carried out first with anhydrous ethyl alcohol and acetone. In both these solvents no solid silver compound was found to be deposited on the anode. Experiments were next repeated with mixtures of alcohol – water and acetone – water.

In aqueous alcohol solutions the formation of peroxynitrate is completely suppressed until alcohol concentration becomes very small. Even in a 3.125% alcohol solution, only a small amount of the solid is formed. The suppression of peroxynitrate formation is accompanied with the formation of copious quantities of the oxidation products of alcohol, viz., acetaldehyde, acetic acid and even carbon dioxide.

In the case of aqueous acetone solutions, however, the suppression of peroxynitrate formation is much less probably because acetone is much more difficult to oxidise. The results are summarised in Table IV.

TABLE IV

Conc. of electrolyte = N-$AgNO_3$. Current density = 110 milliamps /cm^2.
One ampere-hour current passed in all cases.

Solvent.	Wt. of deposit.	%Ag in deposit.
3.125% Alcohol	0.11 g.	78.88
95 % Acetone	0.70	79.10
75 % ,,	2.10	80.20
50 % ,,	2.55	79.40
25 % ,,	3.10	78.80

The figures in the last vertical column leave no doubt regarding the composition of the anodic product. Apart from the question of the current efficiency of its deposition, the product is the same as in the absence of alcohol and acetone.

Mechanism of the Anodic Reaction.—It has been observed earlier in the paper that the anode discharge potentials and the current-potential curves indicate that any reactions observable on the anode seem to follow the primary discharge of nitrate ions. The formation of higher valence silver compounds could therefore be due to reactions between free nitrate radicals and silver ions, probably according to the mechanism :

$$Ag^+ + NO_3 \longrightarrow Ag^{2+} + NO_3^- \quad \text{and}$$
$$Ag^+ + 2NO_3 \longrightarrow Ag^{3+} + 2NO_3^-$$

Followed by

$$Ag^{2+} + H_2O \longrightarrow AgO + 2H^+ \quad \text{and}$$
$$2Ag^{3+} + 3H_2O \longrightarrow Ag_2O_3 + 6H^+$$

Ag_3O_4 may be regarded as $AgO.Ag_2O_3$ complex and two such complex molecules together seem to imbibe one $AgNO_3$, forming the complex $(Ag_3O_4)_2.AgNO_3$.

All these reactions obviously take place rapidly and heterogeneously on the anode. The formation of the solid anodic product is undoubtedly due to the presence of a large number of water molecules surrounding the anode, favouring the hydrolysis of higher valence silver ions, and the absence of easily oxidisable substances like alcohol. The heterogeneous reaction between Ag^{2+} or Ag^{3+} and alcohol would thus appear to take place more rapidly than the hydrolytic reaction, as even 5% alcohol is quite sufficient to suppress peroxynitrate formation.

PHYSICAL CHEMISTRY LABORATORY,
COLLEGE OF SCIENCE, NAGPUR, M.P.

Received March 6, 1956.

[Jour. Indian Chem. Soc., Vol. 33, No. 8, 1956]

CHEMISTRY OF ALIPHATIC THIOCARBAMIDES. PART V. N.N:N'-TRIMETHYLTHIOCARBAMIDE

By Ranbir Singh

Chemistry of N:N:N'-trimethylthiocarbamide has been investigated with respect to its formation and interaction with acids, alkalies, desulphurising agents, silver nitrate, bromine, iodine, nitrous acid, acetic anhydride and benzyl chloride.

N:N:N'-Trimethylthiocarbamide was prepared by the condensation of methyl mustard oil and dimethylamine according to Hofmann's procedure (*Proc. Roy. Soc.*, 1874, **17**, 72). A general examination of the chemistry of this compound has been undertaken.

In its behaviour towards hydrolytic reagents, it resembles other aliphatic thiocarbamides (this *Journal*, 1953, **30**, 499, 695; 1954, **31**, 355,628), although it is more stable. Since it lacks the necessary number of potentially mobile hydrogens, it is not desulphurised with the usual desulphiding agents like mercuric oxide, alkaline lead acetate, etc. (Dixon, *J. Chem. Soc.*, 1893, **63**, 318). When boiled with a strong solution of sodium zincate, however, zinc sulphide is formed in considerable quantity. With aqueous silver nitrate it forms complex compounds, where four or five molecules of silver nitrate combine with two or three molecules of trimethylthiocarbamide. Depending on the relative quantities of the reactants and the experimental conditions, higher or lower complexes are obtained (vide Experimental). Like other aliphatic thiocarbamides, on oxidation with bromine and other oxidising agents it forms the corresponding 'formamidine disulphide' salt. With acetic anhydride and benzyl chloride in the usual way, *N*-acetyl and *S*-benzyl derivatives respectively are obtained (cf. Dixon and Hawthorne, *J. Chem. Soc.*, 1907, **91**, 128, 144).

Experimental

Formation.—Methyl mustard oil (36 g.) and dimethylamine (25 g.) were condensed in alcohol medium. The residue after evaporating off the alcohol was crystallised twice from alcohol, m.p. 87°, yield 53 g. corresponding to 90%. (Found: N, 23.69; S, 27.0. $C_4H_{10}N_2S$ requires N, 23.73; S, 27.11 per cent). The molecular weight was determined cryoscopically using water as the solvent; 0.436 g. of the substance in 25 c.c., 30 c.c. and 35 c.c. water recorded depression of 0.265°, 0.230° and 0.19° respectively, corresponding with molecular weights 118.74, 113.7 and 118.7.

Hydrolysis.—Trimethylthiocarbamide (1.18 g.) was heated under reflux for 1 hour with 25 c.c. of *N* and 5*N* suiphuric acid and caustic soda solutions. The decomposition products were estimated as in other cases (this *Journal*, 1953, **30**, 499). Only 5*N*-NaOH could decompose it to the extent of affording 43% amine and 41% H_2S.

Desulphurisation.—Trimethylthiocarbamide (0.118 g. in 100 c.c. water) was heated on a water-bath with potassium zincate solution (10 c.c.) for half an hour at 60°, 80° and 100°. After filtering off the zinc sulphide formed, the remaining thiocarbamide in the filtrate was estimated by titrating against $Hg(NO_3)_2$ solution after acidifying it with dilute HNO_3 (*ibid.*, 1953, **30**, 223; 1954, **31**, 355). % Desulphurisation at 60°, 80° and 100° was 0%, 0% and 5.5% respectively.

Reaction with Silver Nitrate.—Aqueous solutions of trimethylthiocarbamide and silver nitrate of various concentrations were mixed at room temperature, at boiling point and at 0°. The results are presented in Table I.

TABLE I

Complex compounds of trimethylthiocarbamide and silver nitrate.

S.No.	$AgNO_3$:Thi.	$AgNO_3$.	Wt. of Timeth. Thi.	Condition of reaction.	Ag-salt ignited.	Ag recovered.	Loss.	Ag : loss. Found.	Ag : loss. Calc.	Compositon.
1	1 : 1	0.425 g.	0.30 g.	Cold	0 3584 g.	0.1484 g.	0.2100 g.	432 :604.8	432 : 602	$3Thi\ 4AgNO_3$
	,,	,,	,,	,,	0 4116	0.1728	0.3288	432 :596.8	,,	,,
2	2 : 1	0.85	0 30	,,	0.2844	0.1188	0.1656	432 :602.8	,,	,,
	,,	3 40	1.18	,,	0.4674	0.1966	0 2708	432 :594 8	,,	,,
	,,	,,	,,	,,	0.3258	0.1356	0.1902	432 :602.8	,,	,,
3	1 : 2	0 425	0.59	,,	0.0622	0.0264	0.0358	432 :586.0	,,	,,
	,,	,,	,,	,,	0.1898	0.0784	0.1114	432 :614.0	,,	,,
	,,	0.85	1.18	,,	0.6374	0.2680	0 3694	432 :595.6	,,	,,
	,,	,,	,,	,,	0.4720	0.1998	0.2522	432 :588.4	,,	,,
4	4 : 1	1.7	0.30	,,	0.3970	0.1566	0.2004	540 :546.0	540 :546	$2Thi.5AgNO_3$
5	1 : 4	0 425	1.18	,,	No precipitate was obtained.					
6	1 : 1			Boiling	,,	,,	,,			
7	1 : 2			,,	,,	,,	,,			
8	2 : 1			,,	,,	,,	,,			
9	1 : 1			0°	0 5304	0.2320	0.2984	540 :694.5	540 : 664	$3Thi.5AgNO_3$
10	4 : 1			,,	0.3618	0.1804	0.1814	540 :543.6	540 : 546	$2Thi.5AgNO_3$

Oxidation.—Equivalent quantities of trimethylthiocarbamide and bromine (both dissolved in chloroform) were mixed. A yellow sticky mass separated which under alcohol became colorless but retained its sticky nature. It could not be obtained in a crystalline form. Its picrate was also sticky. It liberated iodine from aqueous potassium iodide. With alkali it decomposed affording sulphur (cf. 'formamidine disulphide', Werner, *J. Chem. Soc.*, 1912, **101**, 2166, 2180).

Nitrous Acid Interaction.—Trimethylthiocarbamide (3 g.) and 15 c.c. of 5*N* acetic acid were taken in a beaker and cooled in ice. Ice-cooled normal sodium nitrite solution (50 c.c.) was added gradually. An oily liquid separated which being highly unstable could not be further purified. It is presumably $(CH_3)_2N.CS.N(NO)CH_3$.

N-*Acetyl Derivative.*—Trimethylthiocarbamide (2 g.) and acetic anhydride (4 c.c.) were heated along with a little zinc chloride for about 10 minutes, and poured in

water. A white crystalline solid separated which was crystallised from alcohol, m.p. 154°. [Found: N, 17.3; S, 20.2. $(CH_3)_2N.CS.N(COCH_3)CH_3$ requires N, 17.5; S, 20.0 per cent].

S-*Benzyl Derivative*.—Equivalent quantities of trimethylthiocarbamide and benzyl chloride were warmed in 40% alcohol and left on a watch glass. Colorless massive crystals separated, m.p. 146-48°. [Found: N, 13.2; S, 15.15. $C_{11}H_{16}N_2S$ requires N, 13.35; S, 15.31 per cent].

Thanks are due to Dr. R. H. Sahasrabudhey and Professor S. S. Joshi for their interest.

ORGANIC CHEMISTRY SECTION,
COLLEGE OF SCIENCE,
BANARAS HINDU UNIVERSIEY.

Received September 14, 1955

[Jour. Indian Chem. Soc., Vol. 33, No. 8, 1956]

STUDIES ON THE FRIES REARRANGEMENT. PART XVI

By S. S. Tewari and Brajendra Nath Tripathi

The effect of less than a molar proportion of anhydrous aluminium chloride as a catalyst in the Fries rearrangement has been studied. A method of separation of *ortho*- and *para*-hydroxyketones by the chromatographic technique has also been developed.

The effect of more than one molar quantity of the catalyst on the Fries rearrangement has been studied by many workers (Pyman *et al.*, *J. Chem. Soc.*, 1930, 280; Thakor and Shah, this *Journal*, 1946, **23**, 234; Amin and Shah, *ibid.*, 1948, **25**, 377; Tiwari and Tewari, *ibid.*, 1954, **31**, 79). But a search in the literature shows that the effect of lesser amount of the catalyst has not been studied earlier. We have therefore investigated the Fries rearrangement of the acetates of phenol, 3-methylphenol, 3-ethylphenol and 2-chloro-4-*tert.*-butylphenol, using 0.25 *M*, 0.5 *M*, 0.75 *M*, 1.0 *M* and 1.25 *M* of anhydrous aluminium chloride.

It has been found that even with 0.25 *M* of the catalyst, the total yields of the hydroxyketones are 72-80%. This observation contradicts the usual notion that one mole of the catalyst is required for the Fries migration of one mole of an ester. With lesser amounts of the catalyst, the yields of *para*-hydroxyketone increase with the catalyst concentration. This observation is also contrary to that of Ralston (*J. Org. Chem.*, 1940, **5**, 645) that beyond the region of one molar quantity of the catalyst, the yield of *para* isomer diminishes with increase in the catalyst concentration.

Experimental

Fries Rearrangement of the Ester.—The ester (1.0 *M*) was rearranged by appropriate amount of anhydrous aluminium chloride at 130° for 2 hours, following the procedure of Tiwari and Tewari (*loc. cit.*). In the first three cases, the separation of *ortho* and *para* isomers was effected by steam-distillation. In a few cases only traces of *para* isomers were found to be present. The results are summarised in Table I.

Table I

Effect of lesser amount of catalyst.

Temp. = 130°. Time = 2 hours.

Catalyst conc.	Yields of hydroxyketones.						
	ortho.	*para.*	*ortho.*	*para.*	*ortho.*	*para.*	*ortho.*
	1. Phenyl acetate.		2. 3-Methylphenyl acetate.		3. 3-Ethylphenyl acetate.		4. 2-Chloro-4 *tert.*-butylphenyl acetate.
0.25 *M*	80.0%	Trace	72.0%	6.0%	74.0%	Trace	72.0%
0.50	82.0	,,	72.0	8.0	78.0	,,	74.0
0.75	80.0	4.0%	70.0	10.0	78.0	,,	74.0
1.00	74.0	10.0	72.0	12.0	80.0	2.0%	80.0
1.25	70.0	18.0	70.0	16.0	80.0	4.0	82.0

Chromatographic Separation of o- *and* p- *Hydroxyketones.*—There are several known methods of separation of *ortho*- and *para*-hydroxyketones from a mixture of both. Each of these methods has its limitations. Hence, we tried chromatographic separation of these isomers using *flowing chromatogram* technique. The Chromatographic method has no special advantage as it provides approximately the same results.

A tube of 2 cm. in diameter and 60 cm. in length was partly filled with dry chloroform and absorbent alumina was added in it carefully until it settled down and a column of 40 cm. was obtained without any air gap.

About 1.5 g. of the known mixture, prepared authentically, or the rearranged product, dissolved in 8 c.c. of dry chloroform, was added to the column. It was gradually drawn in the column. Fresh portions of dry chloroform were added from time to time so that no air was drawn into the upper portion of the column. As the solution was drawn in, a yellow band developed. At first the percolate was colorless, but as soon as the yellow band touched the lowest part of the column, the colour of the percolate turned yellow. A drop of the percolate was then taken on a filter paper and after evaporation of the solvent a drop of 1% ferric chloride solution was added. A blue colour developed at the spot which indicated the presence of the *o*-hydroxyketones. Whole of the percolate responding to the colour test was collected together and the solvent evaporated on a water-bath, when the *o*-hydroxyketone was obtained.

When the percolate ceased to respond to the colour test for the *o*-hydroxyketone, 20 c.c. portions were collected and the solvent evaporated. Usually the first portion yielded nothing. Next portions yielded solid *para* isomers on evaporation of the chloroform. The process was continued with fresh portions of 20 c.c. each until no solid was obtained. All solid portions were collected together and weighed. The results of both the experiments are summarised below.

TABLE II

Chromatographic separation of authentic mixtures.

Hydroxyketones derived from :	Hydroxyketones taken.		Hydroxyketones recovered.	
	ortho.	*para.*	*ortho.*	*para.*
1. Phenyl acetate	1.24 g.	0.34 g.	1.18 g.	0.32 g.
2. 3-Methylphenyl acetate	1.16	0.37	1.12	0.34
3. 3-Ethylphenyl acetate	1.35	0.12	1.32	0.10
4. 2-*tert.*-Butyl-5-methylphenyl acetate	1.28	0.26	1.24	0.21

TABLE III

Chromatographic separation of rearrangement products.

Hydroxyketones derived from :	Temperature.	% Yield of hydroxyketones by Chromatography.		Steam-distillation.	
		ortho.	*para.*	*ortho.*	*para.*
Phenyl acetate	130°	74.0	21.0	70.0	18.0
3-Methylphenyl acetate	130°	74.0	19.0	70.0	16.0

The authors wish to thank Dr. A. B. Sen for his kind interest in this work.

THE CHEMICAL LABORATORIES,
LUCKNOW UNIVERSITY,
LUCKNOW.

Received November 19, 1954.

[Jour. Indian Chem. Soc., Vol. 33, No. 8, 1956]

DIGESTIBILITY OF CEREAL STARCHES BY TAKA-DIASTASE AND PANCREATIN AT DIFFERENT p_H AND AT 38.5° ± 0.01°

By R. D. Patel and R. S. Patel

The digestibility of cereal starches (bavato, kodari, ghau, chokha, jowar, bajari, moriyo and cheno) by Taka-diastase and pancreatin at different p_H and at 38.5° ± 0.01° has been studied. The optimum p_H for digestibility for all starches has been found to be 6.5. Taka-diastase has better activity than pancreatin. The maximum digestibility of different starches is approximately the same.

Divergent views prevail regarding the digestibility of different grains. Thus, it is believed that in Gujarat green gram is more digestible than wheat (ghau) or rice (chokha), while in U.P., wheat is considered to be more digestible than either gram (chana) or rice. Similarly in U.S.A. and Europe, arrowroot crackers are regarded as the easily digestible products.

The diet of the people of Gujarat is almost entirely vegetarian, and hence, cereals and pulses form vital portion of their daily diet. Starch, which forms the main bulk of carbohydrate in food grains, provides about 50% of the daily requirements of the energy. So it was thought desireable to undertake a systematic study of the digestibility of starches of cereals from Gujarat.

Basu and Sarkar (*Indian J. Med. Res.*, 1935, **22**, 745) studied the action of Taka-diastase on the starches from different varieties of rice, and observed that the different varieties differed in their digestibility. Starch from par-boiled rice is more rapidly digested than that obtained from sun-dried rice, presumably due to dextrinisation. Gorbach (*Fett. Seifen*, 1941, **48**, 308) studied the action of β-amylase on the hydrolysis of bean starch and found the optimum p_H for hydrolysis between 4.8 and 5.0.

The digestibility is studied by two methods. In the biological methods it is carried out with animals by feeding them and studying changes in the metabolites. In the laboratory method, the hydrolysis of starch is studied by converting them into monosaccharides. Laboratory method is simple and the uniformity of condition can be maintained more accurately than with animal experiments.

In the present investigation the hydrolysis of starches of cereals by Taka-diastase and pancreatin has been studied at 38.5° ± 0.01° at different p_H.

Experimental

Weighed amount of the starch sample (0.2 g.) was taken into a 100 c.c. conical flask and 20 c.c. of distilled water added to make a thin paste by keeping the flask in a boiling water-bath for 5 minutes till all the granules of starch had gelatinised. It was then cooled and 20 c.c. of a buffer solution of the required p_H was added, followed by 20 c.c. of the enzyme solution. The enzyme solution was prepared in such a concentration that when 10 c.c. of it was added, the strength of it in the bulk was 0.5%. The flask was kept at 38.5° ± 0.01° for 30 minutes. The enzyme was destroyed by adding 25 c.c. of

Fehling-A solution, succeeded by equal volume of the Fehling-B. The flask was heated on a regulated electric heater. It started boiling within four minutes and boiling was continued for two minutes. The flask was kept covered with a watch-glass during heating. The solution was filtered hot at once through asbestos mat in a porcelain Gooch crucible under suction. The precipitates were washed with hot water till free from either copper sulphate or sodium hydroxide. The asbestos mat was transferred into a conical flask with the aid of a pointed glass rod and 50 c.c. of ferric alum solution was added through the Gooch crucible and the precipitate of cuprous oxide was completely dissolved by vigorous shaking. It was titrated against standard $KMnO_4$ solution, using *o*-phenanthroline as an indicator. The end-point was marked by the change of colour from brown to green. Copper was calculated from the $KMnO_4$ reading. Reducing sugar equivalent to weight of copper was obtained from Hammond's table. A blank determination was also carried out with the same volume of the enzyme and buffer solution as was used with the sample.

Weight of hydrolysable starch = dextrose × 0.93.

TABLE I

Hydrolysis of cereal starches by Taka-diastase at different p_H.

Period of hydrolysis = 30 minutes. Enzyme conc. = 0.5% Temp. = 38.5° ± 0.01°.
(Expressed on the basis of total hydrolysable starch).

p_H.	Bavato.	Kodari.	Ghau.	Chokha.	Jowar.	Bajari.	Moriyo.	Cheno.
			A. With Taka-diastase.					
3.05	31.62%	36.27%	45.57%	38 31%	37.20%	40.50%	37.66%	38 59%
3.72	47.42	48.91	47.89	38 40	40 10	44.10	42.98	43.98
4.35	52.63	53.19	55.05	55.80	46.00	55.00	48.54	46.96
5.00	58.12	54.87	55.33	51.60	51.70	58.69	49.90	51.70
5.80	55.98	53.19	54.59	46.03	50.22	55.98	51.70	50.22
6.50	58.86	54.30	55 98	55.60	52.17	59.08	54.03	53.13
7.02	50.44	50.77	52.35	57.19	46.96	54.10	49.56	51.52
7.65	49.25	45.57	41.85	51.47	41.10	48.60	46.03	44.4
			B. With Pancreatin.					
3.05	...	...	...	...	...	...	...	...
3.72	...	...	...	...	...	...	...	...
4.35	22.32	35.52	38.59	35.34	23.25	28.39	37.20	26.97
5.00	37.20	39.06	40.99	38.59	41.38	46.50	43.24	36.73
5.80	36.72	31.15	39.52	38.13	38.13	45.10	39.90	32.08
6.50	39.06	33 01	41.65	39.06	39.06	45.57	40.92	35.80
7.02	33.06	30.87	37.20	34.87	38.59	40.90	39.99	33.48
7.65	33.94	28.83	32.73	34.13	29.76	39.06	38.59	30.96

DISCUSSION

Gorbach (*loc.cit.*) found the optimum p_H for the hydrolysis of bean starch between 4.8 and 5.0. The value rapidly falls on both sides. In the case of cereal starches we have found higher activity at p_H 5.0 and 6.5 with both the enzymes. It is also to be

noted that between these two enzymes there is no marked difference in digestibility, so far as their maximum activity on starch is concerned, though the course it is slightly different.

FIG. 1
Jowar with Taka-diastase.

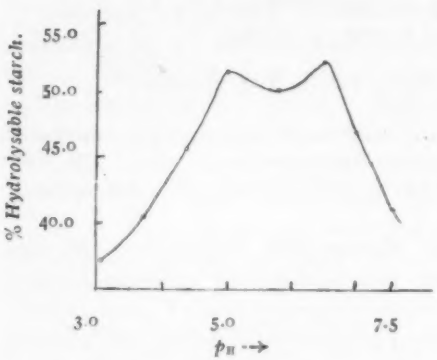
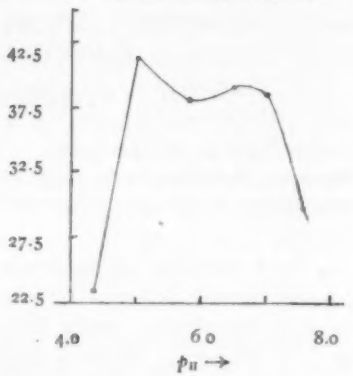


FIG. 2
Jowar with pancreatin.



From Figs. 1 and 2 it can be seen that the hydrolysis is rapid at first and then it falls in the region of p_H 5.5 to 5.8 and it rises up to 6.5, ultimately showing a uniform fall. This suggests that the breakdown of the starch molecules is very rapid on acidic side towards neutral point. It is also to be noted that pulse starches do not hydrolyse at p_H below 4.0. The same is the behaviour of cereal starches. The percentage of hydrolysable starch is higher in the case of Taka-diastase than that in the case of pancreatin at corresponding p_H values, showing that it depends upon the type and activity of the enzyme.

According to Pronin (Zapiski Voronezh Selskoshoz Inst. 19 No. 1, 1941, 177-83 ; *Kim. Ref. Zhar*, 1941, **4**, No. 6, 53) the velocity of saccharification of starch by diastase is related to the phosphorus content, but, so far as cereal starches are concerned, it has been found that such is not the case.

It is also observed that the grain size has some effect on the digestibility, and the results agree to the statement made by Basu *et al.* (*loc.cit.*) that the digestibility differs according to the fineness of the starch grain.

It is a common belief that the digestibility differs from starch to starch but from the experimental results it can be seen that it is practically the same for every starch.

CHEMISTRY DEPARTMENT,
SARADAR VALLABHBHAI VIDYAPITH,
VALLABH VIDYANAGAR,
VIA-ANAND, BOMBAY STATE.

Received January 9, 1956.

[Jour. Indian Chem. Soc., Vol. 33, No. 8, 1956]

CONDENSATIONS OF ARYLDIAZONIUM SALTS WITH REACTIVE UNSATURATED COMPOUNDS. PART VIII. ACTION OF ARYLDIAZONIUM CHLORIDES WITH β-4-METHOXY- AND β-3:4-DIMETHOXYBENZOYLACRYLIC ACIDS

By Hari Shanker Mehra and Kunj Behari Lal Mathur

Aryldiazonium chlorides afford 4′-methoxy- and 3′-:4′-dimethoxy chalkones when coupled under Meerwein's conditions with β-4-methoxy- and β-3:4-dimethoxybenzoylacrylic acids. The latter two acids seem to undergo reaction more satisfactorily than the parent acid in the Meerwein reaction.

In a previous investigation (Mehra and Mathur, this *Journal*, 1955, **32**, 465), β-benzoylacrylic acid was allowed to react with various diazonium chlorides having a negative substituent, under Meerwein's conditions (Meerwein *et al.*, *J. prakt. Chem.*, 1939, *ii*, **152**, 251). It was reported that decarboxylation occurred during the coupling reaction, resulting in the formation of chalkones, thus:

$$PhCO.CH=CH.COOH + ArN_2Cl = Ph.CO.CH=CH.Ar + N_2 + HCl + CO_2 \quad (I)$$

The chalkones could be recovered by extraction of the complex reaction products with aqueous potassium bisulphite or e.g., in the case of the nitrochalkones, with 80-85% sulphuric acid. Yield of chalkone was good in reactions with *p*-chloro- and *p*-nitrobenzenediazonium chlorides and poor with *m*- and *o*-chlorodiazonium compounds. The Meerwein reaction has now been studied with β-4-methoxy- and β-3:4-dimethoxybenzoylacrylic acids.

Benzene, *p*- and *o*-chloro-, *p*- and *o*-bromo-, *p*-, *m*- and *o*-nitro-benzenediazonium chlorides have been allowed to react with 4-methoxybenzoylacrylic acid. Benzene, *p*-, *m*- and *o*-nitrobenzenediazonium chlorides have also been allowed to react with 3:4-dimethoxybenzoylacrylic acid. In every case decarboxylation occurs during coupling which can be represented in a way analogous to the reaction (I.). The chalkones have been recovered as described in our earlier communication (*loc. cit.*). The products from 4-methoxybenzoylacrylic acid are listed in Table I and those from 3:4-dimethoxybenzoylacrylic acid, in Table II. 4-Nitro-, 3-nitro- and 2-nitro-3′:4′-dimethoxychalkones are new products. Also, the syntheses of the last three chalkones, needed for comparison, have been recorded for the first time from 4-, 3-, and 2-nitrobenzaldehydes and 3:4-dimethoxyacetophenone respectively.

Due to the presence of considerable amount of byproducts, presumably some dimeric forms of the chalkones, in the reaction mixture, a strict evaluation of the reactivity of the methoxybenzoylacrylic acids has not been possible. It is significant, however, to note that benzenediazonium chloride, which is generally less reactive, can couple to furnish 7-8% yield of 4′-methoxy- and 3′:4′-dimethoxychalkones.

EXPERIMENTAL

4-Methoxy- and 3:4-dimethoxybenzoylacrylic acids were prepared by the reaction of anisole and veratrole respectively with maleic anhydride in the presence of anhydrous $AlCl_3$ (vide Dave and Nargund, *J. Univ. Bombay*, 1938, **7**, Part III, 191).

Syntheses of 4-Nitro- 3-Nitro-, and 2-Nitro-3′:4′-dimethoxychalkones.—4-Nitrobenzaldehyde (2 g.) and 3:4-dimethoxyacetophenone (2.6 g.) were dissolved in alcohol (12 c.c.) and then treated with 10 drops NaOH solution (conc.). Crystals of *4-nitro-3′:4′-dimethoxychalkone* appeared after sometime. These were filtered, washed with alcohol and recrystallised from benzene, m.p. 180°. (Found: C, 64.62; H, 4.95. $C_{17}H_{15}O_5N$ requires C, 65.2; H, 4.8 per cent). In the same way were prepared *3-nitro-3′:4′-dimethoxychalkone*, m.p. 128° (Found: C, 65.1; H, 4.7. $C_{17}H_{15}O_5N$ requires C, 65.2; H, 4.8 per cent) and *2-nitro-3′:4′-dimethoxychalkone*, m.p. 147-48° (from alcohol) (Found: C, 64.5; H, 4.88. $C_{17}H_{15}O_5N$ requires C, 65.2; H, 4.8 per cent).

Coupling reactions.—The reactions were done as in experiments with benzoylacrylic acid (*loc. cit.*). The amine (*M*/40), dissolved in 25% HCl (9 c.c.) was diazotised with sodium nitrite (1.90 g.) and the diazotised solution (*ca.* 20 c.c.) added to a solution of 4-methoxy- or 3:4-dimethoxy-benzoylacrylic acid (*M*/40) in acetone (30 c.c.) containing also powdered sodium acetate (8 g.) and copper chloride (1g. in 5 c.c. H_2O). There was brisk effervescence which lasted for 2 to 3 hours. The evolved gases, when led through baryta water, precipitated $BaCO_3$. After keeping overnight, the reaction mixture was steam-distilled, and the green aqueous layer in the distilling flask decanted over. The semisolid mass was digested with cold 2*N*-alkali. The alkali-insoluble matter was boiled with saturated potassium bisulphite solution (*ca.* 20 c.c.), coolod, diluted with water (20 c.c.) and filtered. The filtered sulphite liquor was basified with strong aqueous caustic soda (60%). The chalkones were precipitated which were crystallised out from the appropriate solvents.

In the case of the nitrochalkones, the alkali-digested matter was extracted with 85% H_2SO_4 and the acid extract filtered through glass wool over crushed ice. From the benzene solution of the crude nitrochalkones, the tarry matter was separated by precipitation with petroleum ether and filtration. The benzene-petroleum ether solution on concentration yielded products which on further crystallisation from ethanol or methanol furnished the pure nitrochalkones. In the case of 2-nitro-4′-methoxychalkone, however, addition of petroleum ether to the benzene solution of the crude product precipitated the chalkone directly. This was recrystallised from alcohol.

The quantities of the reactants for the coupling reactions (*vide supra*) were adjusted according as *M*/60 or *M*/80 quantities of the methoxybenzoylacrylic acids were used.

The semisolid masses, left after digestion wtth cold 2*N*-alkali, invariably had a certain amount of ether-iusoluble matter. The latter developed a carmine-red colour with H_2SO_4 (conc.), indicating the presence of dimeric forms of chalkones also in the reaction mixture (cf. Stobbe and Breamer, *J. parkt. Chem.*, 1929, *ii*, **123**, 43).

TABLE I

Interaction of various diazonium chlorides with 4-methoxybenzoylacrylic acid.

$CH_3O.C_6H_4.CO.CH = CH.C_6H_4.X$ (chalkone).

Amine diazotised.	NaOH-insol. matter.	Yield.		X=	Cryst. shape & solvent.	M.P.	
						Found.	Lit
Aniline (*M*/80)	1.9 g.	0.20 g.	7.0%	H	EtOH; light yellow needles. [1]	106°	105-106°
p-Chloroaniline (*M*/40)	5.6	0.91	13.3	4-Cl	Ethyl acetate; slightly yellow plates. [2]	130-31°	130-31°
o-Chloroaniline (*M*/40)	4.9	0.85	12.4	2-Cl	Petroleum ether; yellow plates. [3]	92°	91.5-92°
p-Bromoaniline (*M*/80)	2.7	0.41	10.3	4-Br	EtOH; yellow flakes. [4]	153°	152-53°
o-Bromoaniline (*M*/80)	2.5	0.37	9.3	2-Br	EtOH; yellow-white needles. [5]	78°	79.5°
p-Nitroaniline (*M*/40)	4.6	1.60	22.6	4-NO_2	Do; yellow needles. [6]	169°	169°
m-Nitroaniline (*M*/40)	4.9	0.73	10.3	3-NO_2	Do; light yellow needles. [7]	153°	152-53°
o-Nitroaniline (*M*/80)	1.3	0.60	8.4	2-NO_2	MeOH; brown-yellow needles. [8]	111-13°	113°

1. Staudinger and Kon, *Annalen*, 1911, **384**, 123. It may be remarked that diazotised aniline affords only traces of chalkone in its reaction with benzoylacrylic acid (unpublished result).
2. Straus and Blankenhorn, *ibid*, 1918, **415** 254.
3. Pfeiffer *et al.*, *J. prakt. Chem.*, 1928, *ii*, **119**, 122.
4. Percy Barnes *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 3135.
5. Pfeiffer *et al.*, *J. prakt. Chem.*, 1928, *ii*, **119**, 124.
6. Kaufmann, *Ber.*, 1921, **54**, 800.
7. Pfeiffer, *J. prakt. Chem.*, 1925, *ii*, **109**, 46.

TABLE II

Interaction of various diazonium chlorides with 3:4-dimethoxybenzoylacrylic acid.

$(CH_3O)_2.C_6H_3.CO.CH = CH.C_6H_4.X$ (chalkone).

Amine diazotised.	Yield		X=	Cryst. shape & solvent.	M.P. & mixed M.P.
Aniline (*M*/40)	0.50 g.	8.1%	H	Pet. ether and ethyl acetate; yellow crystals.	*83-84°
p-Nitroaniline (*M*/60)	1.10	21.2	4-NO_2	Alcohol.	179°
m-Nitroaniline (*M*/60)	1.15	22.1	3-NO_2	Do	126-27°
o-Nitroaniline (*M*/60)	1.20	23.1	2-NO_2	Do	146-47°

* Kaufmann and Kiser (*Ber.*, 1913, **46**, 3797) record m.p. 85°.

The authors desire to thank Prof. T.R. Seshadri, Ph.D., F.R.I.C., F.A.Sc., F.N.I., Head of the Department of Chemistry, University of Delhi, for his interest in this work and facilities.

CHEMISTRY DEPARTMENT,
UNIVERSITY OF DELHI
DELHI-8.

Received January 24, 1956

[Jour. Indian Chem. Soc., Vol. 33, No. 8, 1956]

A NOTE ON THE VOLUMETRIC ESTIMATION OF IODINE IN IODIDE

By Arcot Viswanathan and Sankaranarayana Gireesan

Vogel ("A Text-book of Quantitative Inorganic Analysis", 1948, pp. 441, 447, Longmans-Green and Co., New York) recommends two volumetric methods of estimating iodide in the absence of other halides, involving the use of potassium iodate or ceric sulphate and large quantities of concentrated hydrochloric acid. In the method herein described, less expensive and more commonly available materials are employed to estimate the iodide. Other halides, even if present, do not interfere with the results.

Reagents used are: (*i*) Standard potassium dichromate (B.D.H., A.R.), 5 g./litre = 0.10.20*N*. (*ii*). Sodium thiosulphate, 0.0998*N*. (*iii*) Standard *N*/10-KI solution (B.D.H., A.R), previously dried over sulphuric acid in a desiccator for a week or longer. (*iv*) Dilute sulphuric acid (8*N*). (*v*) Glycerol (pure, water-white; Lever Bros.). (*vi*). Chloroform or carbon tetrachloride. (pure). All solutions were prepared in distilled water (5 c.c.), boiled free of air.

Procedure.—KI solution (25 c.c.) was pipetted out into a 500 c.c. bottle carrying a tight fitting stopper. The potassium dichromate was added from a burette in slight excess (the required volume being calculated from the assumed normality of the iodide solution), the excess being limited to 2 or 3 c.c. Then dilute sulphuric adid (5 c.c.) was added and the bottle was stoppered, shaken and set aside in the dark for about 5 minutes for the complete oxidation of the iodide to iodine. Now, a well-shaken mixture of 30 c.c. of the sulphuric acid and 5 c.c. of the glycerol was added, washing the sides of the bottle, which was then stoppered, shaken and set aside in the dark. In about 15 minutes' time, the excess dichromate was completely reduced by the glycerol. Chloroform or carbon tetrachloride (5 c.c.) was added and the free iodine was titrated against the thiosulphate with continual shaking of the stoppered bottle. The end-point was cautiously approached, adding the solution from the burette dropwise, vigorously shaking the stoppered bottle after each addition. The end-point was reached when the violet colour of organic layer was discharged. Representative titre values are shown in Table I.

Table I

	KI.	$K_2Cr_2O_7$.	Thio.	Wt. of KI in 1 litre. Calc.	Taken.	Deviation
A	25 c.c.	28 c.c.	26.4 c.c.	17.50 g.	17.60 g.	−0.6 %
B	25	27	25.2	16.70	16.80	−0.6
C	25	20	18.8	12.46	12.52	−0.5
D	25	28	25.9	17.16	17.20	−0.23

Though the deviations from the correct values are less than 1%, the low values (of A, B and C) are due to traces of moisture, persisting in the salt. Sample D furnished the best value as it was desiccated for a longer duration than the other samples.

The choice of the reducing agent is limited by several considerations. The reduction of dichromate should be effected at room temperature (30°) lest any application of heat to hasten the reaction should volatilise the iodine. At the same time, the reagents added or their oxidation products should be such that they would not consume any iodine. Of the several compounds tried, glycerol, under the conditions of the experiment, was found to be the best and was smoothly oxidised to carbon dioxide (Welwart, *Seifens. Ztg.*, 1936, **63**, 372). A large excess of the dichromate is avoided as it requires considerable time to be reduced by the glycerol. In repeating the titrations of an iodide solution, the minimum excess (say of 1 c.c.) of the dichromate required, may be determined by calculation from a previous titre value and the normalities of the solutions. It may be mentioned that the addition of even 2 g. of potassium bromide initially to the iodide solution does not interfere with the titre value.

The authors are indebted to Prof. Lourdu M. Yeddanappalli. S. J., for his keen interest in the work and for facilities provided.

CHEMICAL LABORATORIES,
LOYOLA COLLEGE,
MADRAS-31.

Received May 23, 1956.

PRESIDENT :

B. C. GUHA, D.Sc., PH.D., F.N.I.

VICE-PRESIDENTS :

(who have filled the office of President)

N. R. DHAR, D.Sc., DR.ES.SC., F.R.I.C., F.N.I.
B. B. DEV, D.Sc., F.R.I.C., F.N.I.
SIR J. C. GHOSH, KT., D.Sc., F.N.I.
P. C. GUHA, D.Sc., F.N.I.
J. N. MUKHERJEE, C.B.E., D.Sc., F.A.S.B., F.N.I.
MATA PRASAD, D.Sc., F.R.I.C., F.N.I.
J. N. RAY, O.B.E., D.Sc., F.R.I.C., F.N.I.
P. RÂY, M.A., F.N.I.
B. K. SINGH, Sc.D., F.R.I.C., F.N.I.

VICE-PRESIDENTS :

U. P. BASU, D.Sc., F.N.I.
B. SANJIVA RAO, D.Sc., PH.D., F.N.I.
K. VENKATARAMAN, D.Sc., PH.D., F.R.I.C., F.N.I.
D. B. LIMAYE, M.Sc.,
President of Poona Branch (*ex-officio*)

HONY. SECRETARY :

S. K. MUKHERJEE, D.Sc.

HONY. TREASURER :

B. N. GHOSH, D.Sc., F.N.I.

MEMBERS OF THE COUNCIL :

D. K. BANERJEE, D.Sc.
P. K. BOSE, D.Sc , F.N.I.
D. CHAKRAVARTI, D.Sc., F.N.I.
MRS. ASHIMA CHATTERJEE, D.Sc.
B. CHATTERJEE, D.Sc.
A. C. CHATTERJI, D.Sc., DR. ING., F.N.I.
H. N. DAS GUPTA, D.Sc.
R. D. DESAI, D.Sc., F.R.I.C., F.N.I.
S. S. JOSHI, D.Sc., F.R.I.C., F.N.I.
M. N. GOSWAMI, M.A., DR.ÈN.CH.
T. N. GHOSH, D.Sc., F.N.I.
J. GUPTA, D.Sc.
A. N. KAPPANNA, D.Sc , F.N.I.
R. P. MITRA, D.Sc., F.N.I.
S. M. MUKHERJI, D.Sc., Ph.D.
P. V. NAIR, M.Sc., D.PHIL.
A. B. SEN, M.Sc., PH.D.
V. SUBRAHMANYAN, D.Sc., F.R.I.C , F.N.I.
L. M. YEDDANAPALLI, M.A., Ph.D., D.Sc., F.R.I.C.
S. H. ZAHEER, M.A., PH.D.

HONY. EDITORS :

S. R. PALIT, D.Sc., F.R.I.C., F.N.I.
R. C. SHAH, D.Sc., F.N.I.

BOARD OF ASSOCIATE EDITORS :

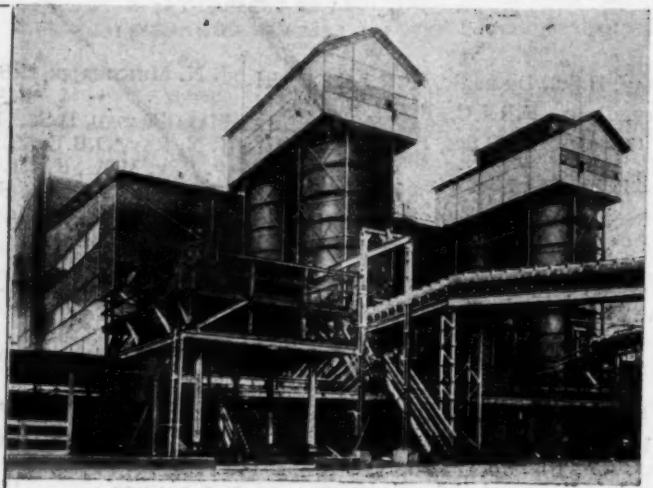
D. K. BANERJEE, D.Sc.
P. K. BOSE, D.Sc., F.N.I.
B. CHATTERJEE, D.Sc.
J. K. CHOWDHURY, M.Sc., PH.D., F.N.I.
P. C. DUTTA, D.Sc.
B. N. GHOSH, D.Sc., F.N.I.
J. C. GHOSH, D.Sc., F.N.I.
A. N. KAPPANNA, D.Sc., F.N.I.
S. K. MUKHERJEE, D.Sc.
B. C. GUHA, D.Sc., PH.D., F.N.I.
P. RAY, M.A., F.N.I.
T. R. SESHADRI, M.A., PH.D., F.N.I.
P. B. SARKAR, DR.ES. SC., F.N.I.
K. VENKATARAMAN, D.Sc., PH.D., F.N.I.

HONY. AUDITORS :

P. C. NANDI, M.A., B.Sc., A.C.A.R.A.
A. B. GUPTA, B.Sc., L.L.B., A.C.A.R.A.

ASST. SECRETARY:
B. C. ROY, M.Sc.

ASST. EDITOR :
G. BANERJEE, M.Sc.



WE DESIGN
DELIVER &
ERECT

COMPLETE EQUIPMENT FOR H_2SO_4 PRODUCTION

WE SHALL OFFER TO YOU TECHNICAL UNITS
OF THE FOLLOWING OUTPUTS:

Raw material: SULPHUR		PYRITE	
10 mt/24 hrs.		50 mt/24 hours	
25 mt/24	,,	100 mt/24	,,
50 mt/24	,,	150 mt/24	,,

WE SHALL GUARANTEE A SUITABLE
AND UP-TO-DATE DESIGN AND ECONOMIC OPERATION

TECHNOEXPORT

Praha--Czechoslovakia

For informations please contact

TRADE REPRESENTATION OF CZECHOSLOVAK REPUBLIK,

BOMBAY BRANCH: KASTURI BUILDING, JAMSHEDJI TATA ROAD, BOMBAY.

CALCUTTA BRANCH: P-38, MISSION ROW EXTN., CALCUTTA.

WHAT'S *NEW* IN "QUICKFIT"?

"QUICKFIT" ROTARY FILM EVAPORATOR

1. This all-glass apparatus operates under vacuum and rotates on rollers.
2. The original solution is heated in a water bath whilst the receiving flask is cooled in a freezing mixture thus achieving rapid concentration.
3. It is designed to evaporate thermo-sensitive solution (such as solutions obtained by the Craig Counter Current technique) down to small bulk in batch quantities upto 350 ml.

ACCREDITED DISTRIBUTORS:

UNION SCIENTIFIC SYNDICATE

DEVKARAN MANSION, 71, PRINCESS STREET, BOMBAY 2

Tel : 28465 Gram : 'PETROLIUM'

For Laboratory *Reagent Quaility* Acids

To Precise Specifications

Maximum Limits of Impurities:	Acid Sulphuric H_2SO_4 :98% w/w Sp. gr. 1.840 at 15°.	Acid Nitric HNO_3:69.8% w/w Sp.gr. 1.420 at 15°.	Acid Hydrochloric HCl:35.39% w/w Sp. gr. 1.8 at 15°.
Non-Volatile Matter :	0.0025 %	0.001 %	0.0015 %
Chloride (Cl) :	0.0003 %	0.0001 %	—
Free Chlorine (Cl) :	—	—	0.0002 %
Nitrate (NO_3) :	0.00002 %	—	—
Iodate (IO_3) :	—	0.0005 %	—
Sulphate (SO_4) :	—	0.0003 %	0.0003 %
Heavy Metals (Pb) :	0.0002 %	0.0002 %	0.0002 %
Iron (Fe) :	0.0001 %	0.0001 %	0.0001 %
Arsenic (As_2O_3) :	0.00001 %	0.05 part per million	0.04 part per million
Ammonia (NH_3) :	0.0005 %	—	—
Oxygen Absorbed (O) :	1.0001 %	—	—

We invite orders and enquiries.
Write us about your requirements
for other reagent quality chemicals.

Bengal Chemical & Pharmaceutical Works, Ld.

CALCUTTA :: BOMBAY :: KANPUR

Office : 6, Ganesh Chunder Avenue, Calcutta-13

All in One
INDEX
REAGENT BOTTLES
made by
Sigcol

Sole Distributors—
GHARPURE & CO.
P36, ROYAL EXCHANGE PLACE
EXTENSION • CALCUTTA-1
GRAM: MEENAMO PHONE: 22-2081

VERY RELIABLE INDIGENOUS SUBSTITUTES
OF GUARANTEED ANALYTICAL REAGENTS
MAY BE FOUND IN

"BASYNTH"
Brand
ANALYTICAL REAGENT

Acid Hydrochloric
Acid Hydrochloric Fuming
Acid Sulphuric
Acid Nitric
Acid Nitric Fuming
Acid Acetic Glacial
Ammonium Hydroxide
Benzene
Toluene
Xylene
Petroleum Ether
Amyl Alcohol
Butyl Alcohol Etc., Etc.

BASIC & SYNTHETIC CHEMICALS PRIVATE LTD
P. O. Jadavpur College, Calcutta-32

GAS PLANTS
FOR
Chemical & Metallurgical
LABORATORY INDUSTRY
*
installed at leading
Colleges and Laboratories

GANSONS
PRIVATE LIMITED.
P.O.B. 5576, BOMBAY-14.
——Also makers of——
Superior Laboratory Fittings
Atomic Equipments.

* OIL GAS PLANTS
* WOODEN FURNITURE
for Homes, Offices &
LABORATORIES
* SCIENTIFIC APPARATUS & INSTRUMENTS

MANSFIELD OIL GAS CO., LTD.,
16, Radhanath Chowdhury Road, Calcutta-15.
301, Linghi Chetty Street, Madras-1.

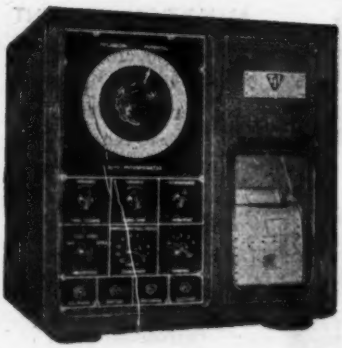
FOR RAPID & ACCURATE CHEMICAL ANALYSIS

USE

TINSLEY POLAROGRAPH

WITH DERIVATIVE CIRCUIT

Here are some advantages:



* MICRO ANALYSIS
* HIGH SENSITIVITY
* QUALITATIVE AND QUANTITATIVE ESTIMATION
* SIMULTANEOUS ESTIMATION OF SEVERAL CONSTITUENTS ON ONE POLAROGRAM
* ADAPTABILITY: ANALYSIS OF METALS, ORGANIC & INORGANIC SUBSTANCES ON THE SAME SAMPLE
* REPEATED ANALYSIS
* SIMPLIFIED OPERATION FOR USE BY SEMI-SKILLED STAFF
* ROUTINE ANALYSIS WITH SPEED AND ACCURACY.

For Further particulars, please contact Sole Agents in India

PIONEER INDUSTRIES

20, British Indian Street, CALCUTTA-1. | 21, Forbes Street, BOMBAY-1. | 193, Mount Road, MADRAS-2.

The 1000A Oscillator and Null Detector

FOR

Conductivity Measurement

This instrument combines in one unit, oscillator, amplifier and phase-sensitive detector with self contained power supply for low frequency Bridge measurement. Independent balance of reactive and resistive components.

Specifications:—		
	Oscillator frequency	100 c. p. s.
	Oscillator output	1 watt. approx.
	Distortion	less than 3%
	Sensitivity	better than 20 micro-volts.

Indication in panel meter as well as by head phones with terminals for operating pen recorders.

Low frequency oscillators. 3 spot frequency of 500 cps., 1000 cps and 2000 cps. for bridge measurement and other Laboratory work.

EMISSION RADIO & VARIETIES.

Manufacturers of: **ELECTRONIC APPLIANCES**

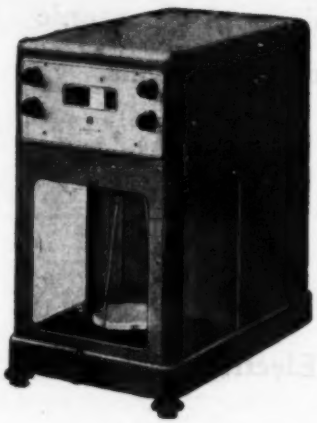
120, LOWER CIRCULAR ROAD, CALCUTTA 14.

HELVETICA CHIMICA ACTA

The HELVETICA CHIMICA ACTA, founded in 1918, publishes in one of the three national languages the principal results of research work in pure chemistry carried out in Switzerland. The HELVETICA CHIMICA ACTA are property of the Swiss Chemical Society. Annually 7-8 numbers are published which members receive without charge.

All correspondence concerning membership of the Swiss Chemical Society or subscriptions for the HELVETICA CHIMICA ACTA should be addressed to :

SWISS CHEMICAL SOCIETY, BASLE 7.



The competent chemist always prefers the

METTLER-ANALYTICAL BALANCE

MADE IN SWITZERLAND

With the following advantages :—

-Automatic operation of the weights up to 200 Grams.

-Large optical scale of 115 Mgs.

-Constant loading of the beam giving highest precision throughout the complete range.

-Reading of the weights on one single scale.

Sole Agents :—

RAJ-DFR-KAR & Co.

COMMISSARIAT BUILDING

HORNBY ROAD,

FORT BOMBAY.

Weight = 123.7306 grams.

-EXACT-QUICK-SURE-SIMPLE.

-Service facilities available at BOMBAY, MADRAS & CALCUTTA.

Telephone. 27304. Telegram : 'Techlab'

Ask for offers and detail literature.

Phone—34-3176. Telegrams—Nadiachemi.

NADIA CHEMICAL WORKS PRIVATE LTD.

C 44, 45 & 46, COLLEGE STREET MARKET, CALCUTTA

Manufacturers of :—

1. *CHEMICALS*—**Benzene, Toluene, &c., Bromine, Halogen derivatives of both Organic and Inorganic compounds and other fine Laboratory Chemicals.**
2. **STILLS for distilling Essential Oils, Alcohols, Water, etc.**

   RECTIFIERS, CONDENSERS, &c.
3. **OVENS, Baths &c for Gas, Oil or Electric heatings.**
4. **Scientific Apparatus (PHYSICAL, CHEMICAL, BIOLOGICAL, &c.) of both Glass and Metal.**
5. **MICRO-ANALYSIS APPARATUS.**

Please ask for Estimates.

Large Stockists of:

Quickfit Interchangeable Standard Joints and Assemblies etc.

and

Manufacturers of any kind of special Glass Apparatus of soft or Pyrex Glass.

Please Enquire to

SCIENTIFIC GLASS APPARATUS MFG. CO.

11/2 Harinath Dey Road, Calcutta-9

Phone : B. B. 4911. Gram : Sigamko,

BOROSIL

LABORATORY GLASSWARE

such as

FLASKS, BEAKERS, CONDENSERS, MEASURING FLASKS, MEASURING CYLINDERS, PIPETTES & ANY SPECIAL APPARATUS MADE TO DESIGN

and

PENICILLIN VIALS, VACCINE BULBS—WHITE & AMBER

ALL OTHER APPARATUS & EQUIPMENT MANUFACTURED TO CLIENT'S DESIGN

INDUSTRIAL & ENGINEERING APPARATUS CO. PRIVATE LTD.

CHOTANI ESTATES, PROCTOR ROAD GRANT ROAD, BOMBAY 7.

Grams: 'LABFURNISH' Phone: 62761

LABORATORY FURNISHERS

Dhun Mansion, Vincent Road, Dadar, BOMBAY-14.

**

AVAILABLE EX-STOCK

**

'QUICKFIT' INTERCHANGEABLE GROUND GLASS JOINT ASSEMBLIES

'CAMBRIDGE' pH METERS: Bench Pat., Portable Pat. & Direct Reading Model. & All types of Electrodes

CAMBRIDGE DIAL THERMOMETERS

** SARTORIUS—BALANCES **

MEMMERT GERMAN ELECTRIC OVENS, IKA GERMAN ELECTIC STIRRERS, ROTOFIX ELECTRIC CENTRIFUGES, AEROGEN PETROL GAS PLANT, ORSATS GAS ANALYSIS APPARATUS Etc.

GARMAN TEMPERATURE INDICATORS

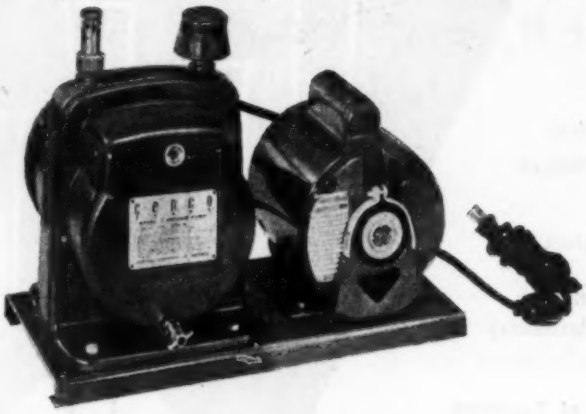
GLASSWARE :- 'PYREX' 'JENA' & WESTGLASS

*

Branch Office: Metilal Mansion, Kapasia Bazar, Ahmedbad 2.

KETJEN
MEKOG
AIME
A.C.Z.
N V
C P
Battery acid
Catalyst, m.s. fluid cracking
Catalyst, m.s. fluid hydroforming
Chloramine
Dioctylphthalate (D.O.P.)
Diphenylolpropane
Oleum
Ortho toluene sulphonamide
Para benzoic sulphonamide
Para toluene sulphochloride
Para toluene suphonamide
Potassium permanganate
Saccharin 550x
Saccharin crystals 450-500x
Sulphur dioxide, liquid
Sulphuric acid 66° Bé
Sulphuric acid, chem. pure
Sales office
of 8 leading
Dutch chemical
industries
Export - Import - Transit
Nederlandsch Verkoopkantoor
voor Chemische Producten N.V.
63 Mauritskade
Amsterdam-Holland
Postbox 4038
Telephone 54322
Telegrams: Chemicals
Telex 12270

NOW
THE VIBRATION'S GONE
.... AND SO IS THE NOISE



THE NEW
CENCO HYVAC—7 HIGH VACUUM PUMP

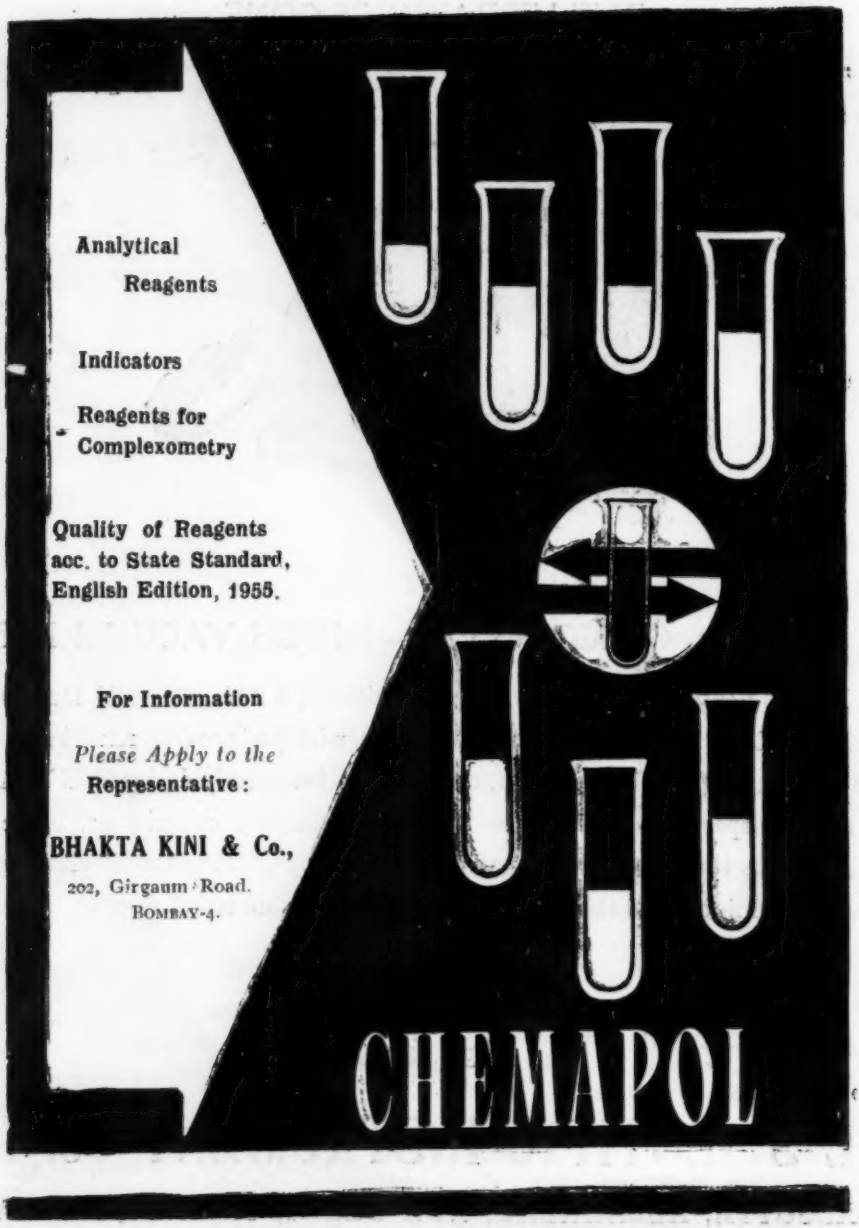
Messrs. Central Scientific Company, makers of a series of world famous and widely popular vacuum Pumps, now come up with yet another remarkable high vacuum pump - the quiet, compact, efficient and beautifully designed HYVAC-7. For the floor space occupied by the pump, its pumping capacity per cubic foot much exceeds that obtainable by many other pumps. Free air displacement is 70 liters per minute and the guaranteed ultimate vacuum is 0.1 micron.

For full particulars write to

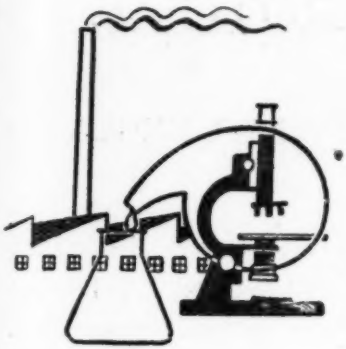
SOLE AGENTS

THE SCIENTIFIC INSTRUMENT Co. Ltd.

CALCUTTA, ALLAHABAD, NEW DELHI, MADRAS, BOMBAY.



PRAHA, CZECHOSLOVAKIA



SERVING for LAST 40 YEARS

Laboratory Chemicals & Reagents

of a wide range are manufactured by us under expert supervision to ensure guaranteed standard & reliability.

A selection from our range :

- Acetone
- Acid Acetic glacial 99-100%
- Alcohol Amyl
- Alcohol Methyl
- Barium Carbonate
- Barium Chloride
- Benedicts' Solution
- Benzene
- Carbon Tetrachloride
- Lead Acetate
- Liquor Ammon Fort (24/27%)
- Magnesium Sulphate XL

THE CALCUTTA CHEMICAL CO., LTD.

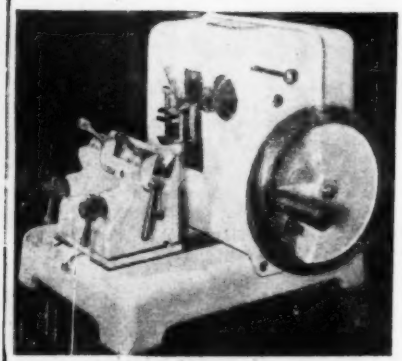
HEAD OFFICE: 35, Panditia Road, Calcutta 29.

BRANCH OFFICES & DEPOTS AT: Delhi, Madras, Bombay, Bangalore, Vizag., Nagpur, Jamshedpur, Patna, Ranchi, Bhagalpur, Madhupur, Asansol, Siliguri.

Regtd. No. C1878

B. T. L. ROTARY MICROTOME

[Ex: M/s BAIRD & TATLOCK (LONDON) LTD. ENGLAND]



This automatic microtome enables the cutting of sections of thickness 1 to 25 microns in steps of 1 micron, the required thickness being selected by an indicator at the front. An automatic locking device locks the wheel at the end of the following revolution and automatically lifts the pinion from the toothed wheel thus preventing damage to the automatic thickness mechanism. This device is very advantageons in removing the object clamp or object stages.

A universal ball stage holder and 2 object stages are provided.
The knife can be adjusted at any angle up to 30 from vertical.

Further details can be had from

SOLE AGENTS:

TOSHNIWAL BROTHERS PRIVATE LTD.

198, Jamshedji Tata Road,
FORT, BOMBAY-1

Branch:
3/7 Mutiny Memorial Road,
NEW DELHI-1.

Branch:
9, Blacker's Road,
Mount Road,
MADRAS-2.

Printed by Sri Sibendranath Kanjilal, Superintendent, Calcutta University Press., 48, Hazra Road., Ballygunge, Calcutta and Published by G. Banerjee, Esq., M.Sc., Asst. Editor., Indian Chemical Society.